University of Alberta

Air Quality and Exposure Monitoring of Sulfur Dioxide in the Community of Fort McKay: A Baseline Assessment

by

Harbinder K. Sunita Ranganathan

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the Master of Science

in

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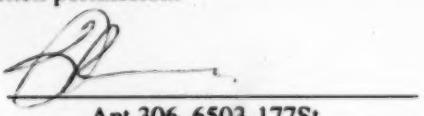

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Air Quality and Exposure Monitoring of Sulfur Dioxide in the Community of Fort McKay: A Baseline Assessment** submitted by **Harbinder K. Sunita Ranganathan** in partial fulfillment of the requirements for the degree of **Master of Science** in **Environmental Science.**

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Abstract

Oil sands operations in northern Alberta yield sulfur dioxide (SO_2) as a by-product. The objective of this study was to measure baseline levels of SO_2 in indoor and outdoor air in Fort McKay, Alberta, in order to assess whether proximity to increased oil sands activities affects air quality in the community.

In fall 1999, 30 households were randomly chosen for indoor and outdoor passive sampling of SO_2. Four-day time weighted levels of SO_2 and air exchange rates were measured.

Indoor levels of SO_2 (n=30; 100% less than level of detection, 1.3 $\mu g/m^3$) were minimal and lower than outdoor levels (n=28; 64% above level of detection; mean: 1.6 $\mu g/m^3$; range: 1.3 to 3.6 $\mu g/m^3$). Thus, oil sands activities during the monitoring period did not increase levels of indoor/outdoor SO_2 to levels intended for human health protection. Air exchange rates (mean: 0.38 air changes per hour; range: <0.01 to 0.73 air changes per hour) were consistent with typical air exchange rates in North American homes.

Dedicated to my family, especially

my husband, Bharat,

and my parents, Sadhu and Sarjit,

for their support and love

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List of Symbols

ACH	Air Exchange per Hour
BPT	Best Practicable Technology
CAT	Capillary Absorption Tube Complex
DQO	Data Quality Objectives
H_2SO_3	Sulfurous Acid
H_2SO_4	Sulfuric Acid
H_2S	Hydrogen Sulphide
LOD	Level of Detection
MRST	Maximum Recommended Sampling Time
NIOSH	National Institute of Occupational Safety and Health
PMCH	Perfluorinated methylcyclohexane
QA	Quality Assessment
QC	Quality Control
RDL	Relative Detection Limit
RSD	Relative Standard Deviation
SF_6	Sulfur Hexafluoride
SO_2	Sulfur Dioxide
SO_3	Sulfur Trioxide
SO_4^{2-}	Sulfate
THE	Total Human Exposure
TWA	Time Weighted Average
σ	Standard Deviation

1.0 Introduction

1.1 Background

The Athabasca oil sands of Alberta are believed to be 200 million years old. It is estimated to contain nearly 600 billion barrels of bitumen. Thus, the Athabasca oil sands represent one third of the world's known petroleum resources. Its reserves are greater than the combined reserves of the Middle East, United States and Western Europe (Kumar, 1979).

During the oil sands operation, sulfur is removed from the bitumen first as hydrogen sulfide (H_2S) and then it is either converted into elemental sulfur or burned to produce sulfur dioxide (SO_2) (WBEA, 1998). The estimated SO_2 emission in Alberta before 1998 is 240 tones per day (Sandhu and Blower, 1986; Colley and Poon, 1982). This has decreased 20% since the adoption of the best practicable technology (BPT) in Alberta from 1974 to 1982 (Sandhu and Blower, 1986; Colley and Poon, 1982). BPT includes construction of taller stacks to enhance greater dispersion of contaminants and ground level monitoring program that regulates industrial operations (Gunn et al., 1995). Other BPT includes removal of 95% of sulfur from coke before it is used to fuel the main boilers, and use of natural gas fired boilers and a new turbogenerator to accommodate the energy requirements of oil sands companies (Colley and Poon, 1982).

Even with adoption of the BPT, residents of the area were concerned with their health as a result of increased oil sands activities over the last ten years. Thus, a study

was conducted to measure the amount of SO_2 in microenvironments (indoor and outdoor air at residences) where people spend the majority of their time.

1.2 Proposed Methodology

A passive monitor was used to monitor the indoor and outdoor concentrations of SO_2. The design of the passive monitor was adapted from a design by Leaderer et al. (1994). Others found that a sampling duration of 24 hours was not long enough. Thus, a sampling duration of 96 hours or 4 days was established (Prince and Robb, 1999). The passive samplers were placed in fixed locations (indoors and outdoors) at 30 residences in Fort McKay, Alberta. These 30 locations were intended to represent spatial variability of SO_2 in the community. One round of sampling was planned in fall 1999. The passive monitors were also placed in an Environmental Monitoring Station in Fort McKay, which is five minutes north of Fort McKay. These results were compared to continuous monitoring results obtained by the Environmental Monitoring Station to assess the accuracy of the passive sampler. Furthermore, the data were used to determine if measurements obtained from the Environmental Monitoring Station were representative of levels of SO_2 in the community. In addition, a *Household Characteristics Questionnaire, Personal Exposure and Activity Questionnaire, Household Activity Questionnaire and Time Activity Survey* were administered to determine indoor sources of SO_2 in the homes.

1.3 Thesis Research

1.3.1 Objective of the Study

The synthetic oil production rate associated with current oil sands activities is less than 300,00 barrels per day. Before year 2002, synthetic oil production is estimated to be less than 400,00 barrels per day. The overall production of synthetic oil is estimated to rise to greater than 800,000 barrels per day as a result of additional mining, extraction, upgrading and tailing ponds operations from proposed and disclosed oil sands activities (Colley and Poon, 1982). With the proposed increase in oil sands activities, there is an increase concern of air quality and the health of the residences in Fort McKay. The objective of this study was to establish baseline indoor and outdoor SO_2 measurements in order to assess whether proximity to increased oil sands activities has an observable effect on the air quality in the community. Baseline SO_2 measurements were taken to represent current air quality in the area. Future measurements will be taken after overall production rates are greater than 800,000 barrels per day. These measurements will be compared to assess whether differences exist between the two time periods.

1.3.2 Data Quality Objectives

Quality assurance programs are intended to reduce measurement errors to tolerable limits and to provide a mean of ensuring that measurements generated have a high probability of being of acceptable quality. There are two concepts of quality assurance-quality control (QC) and quality assessment (QA). QC is mechanism used to control errors. It is based on protocols. These protocols must be rigorously

followed and they should be established for sampling, measurement, calibration and data handling. In addition, the use of blanks and replicates should be part of the sampling protocol (Keith, 1988; Keith et al., 1983; Taylor, 1981). It is recommended that the blanks comprise approximately 10% of the samples collected (NIOSH, 1977). Also, chain-of-custody forms are necessary for assuring positive identification of samples and documentation of the details of the samples. QA incorporates mechanisms used to verify that the system is operating within acceptable limits. The best way to accomplish this is the use of audits (Keith, 1988; Keith et al., 1983; Taylor, 1981).

Quality assurance can define meaningful data quality objectives (DQOs) for the researcher. In order to address DQOs, six data characteristics must be defined: precision, accuracy, representativeness, completeness, comparability and limit of detection.

1.3.2.1 Precision

Precision is defined as how close a result is to the known measurement and is measured by the standard deviation of the data sets. This can be done by either splits or co-located duplicates (Berthouex and Brown, 1994; Nees, 1993; Barth, 1992; Keith, 1991; Kirchmer, 1983; NIOSH, 1977). An acceptable level of precision is +/- 25% as indicated by the National Institute of Occupational Safety and Health (NIOSH) manual (Alberta Health, 1997; NIOSH, 1977, Taylor et al., 1977).

1.3.2.2 Accuracy

Accuracy is a measure of how close the measured value is to the true value. To assess accuracy of the field results, measurements obtained from the standards, spiked samples, reference samples and field audits samples are compared to field results (Berthouex and Brown, 1994; Nees, 1993; Barth, 1992; Keith, 1991; Kirchmer, 1983; NIOSH, 1977). In this study, the standard measurement was the continuous monitoring of SO_2 by the Environmental Monitoring Station in Fort McKay. An acceptable level of accuracy is +/- 25% as indicated by the NIOSH manual (Alberta Health, 1997; NIOSH, 1977, Taylor et al., 1977).

1.3.2.3 Representativeness and Completeness

Representativeness is the reflection of a particular condition at a site by the samples collected. Completeness is the measure of the amount of validated data from a sampling plan. To ensure completeness of the samples, phased sampling can be used, which involves re-sampling of the areas where samples were lost (Barth, 1992; Keith et al., 1983).

1.3.2.4 Comparability

Comparability measurement provides the needed control over the total measurement process to insure that different studies can be compared. This is achieved through quality control in the lab and field audit. Furthermore, proper sampling techniques and sample handling and analysis should be done according to protocol (Barth, 1992; Keith et al., 1983).

1.3.2.5 Level of Detection

The level of detection (LOD) is the level of the contaminant below which there is not a certainty whether it is a result of background noise or sampling error. It is calculated from standard deviation of the blanks (σ) multiplied by a multiple. The multiple used is in accordance with selection of accepted risks of false positives and false negatives. False positives or Type I error is incorrectly rejecting a null hypothesis when it is true. False negative or Type II error is incorrectly failing to reject the null hypothesis when it is false (Berthouex and Brown, 1994; Barth, 1992; Keith, 1991; Keith et al., 1983; Long and Winefordner, 1983). From Table 1.1, a level of 2.33σ for LOD and 4.66σ for relative detection level (RDL) was chosen as acceptable (Keith, 1994). At this level, there is a 1% chance that the signal measured at the LOD or greater would be a result of a random fluctuation of the blank signal (Long and Winefordner, 1983).

Table 1.1 Probability of false positive and false negative determinations (taken from Keith, 1994).

LOD	RDL	False Positives	False Negatives
3 σ	3 σ	0.1 %	50%
3 σ	4 σ	0.1%	16%
3 σ	5 σ	0.1%	2.3%
3 σ	6 σ	0.1%	0.1%
2.33 σ	2.33 σ	1%	50%
2.33 σ	4.66 σ	1%	1%
1.64 σ	3.28 σ	5%	0.5%

LOD= Level of Detection
RDL= Relative Detection Level
σ= Standard Deviation

1.3.3 Study Area Overview

The study area is the community of Fort McKay. Fort McKay is located 55 km north of Fort McMurray as shown in Figure 1.1. It is situated along the west bank of the Athabasca river. The location of Fort McKay relative to oil sands companies is shown in Figure 1.2. It can be seen that the community is within areas of active oil sands production and extraction. The main past-times are boating, hunting, fishing, hockey, cross-country skiing, baseball and skidoing (McKay, 1999). The dominant language in Fort McKay is Cree, Chipewan and English (Statistics Canada, 1999).

The population of Fort McKay is 347. There are 100 dwellings, 75 single-detached and 25 movable dwellings, according to 1996 census (Statistics Canada, 1999). Out of 100 dwellings, 40 dwellings are owned, 15 are rented and 45 are band housing. The employment rate for males is 16% full-time and 35% part-time. The employment rate for females is 9% full-time and 24% part-time (Statistics Canada, 1999). The economic base of Fort McKay is related to the oil and forest industries. Some of the residents are employed by Suncor Inc. and Syncrude Canada Ltd. There is some seasonal work in forestry such as fire fighting and slashing. Hunting and trapping are also used by a few residents as a source of income (McKay, 1999).

Fort McKay is made up of mostly five or more people households. The second most prevalent household type is four to three people per household. The least prevalent household type is two people per household. The highest annual household income earned ranges from $10,000 to $19,999. The second and third most dominant annual household incomes are under $10,000 and $20,000 to $29,999 respectively (Statistics Canada 1999).

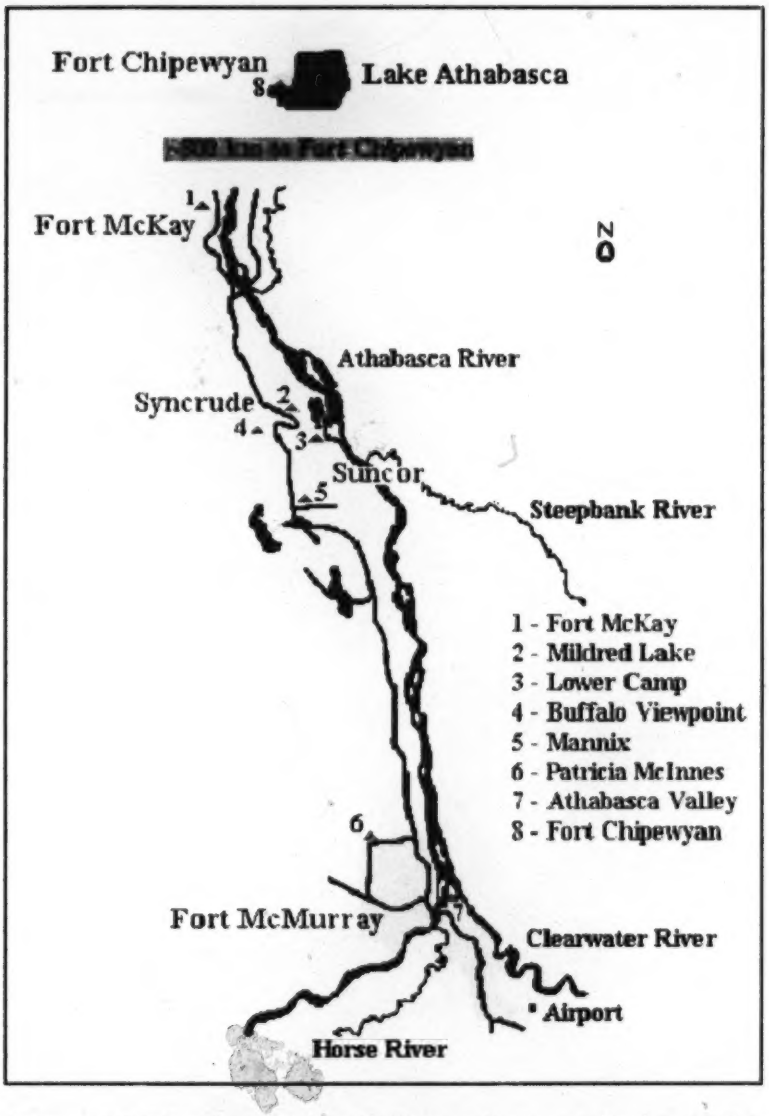


Figure 1.1 Location of Fort McKay and air monitoring stations in the Wood Buffalo Environmental Association monitoring network.

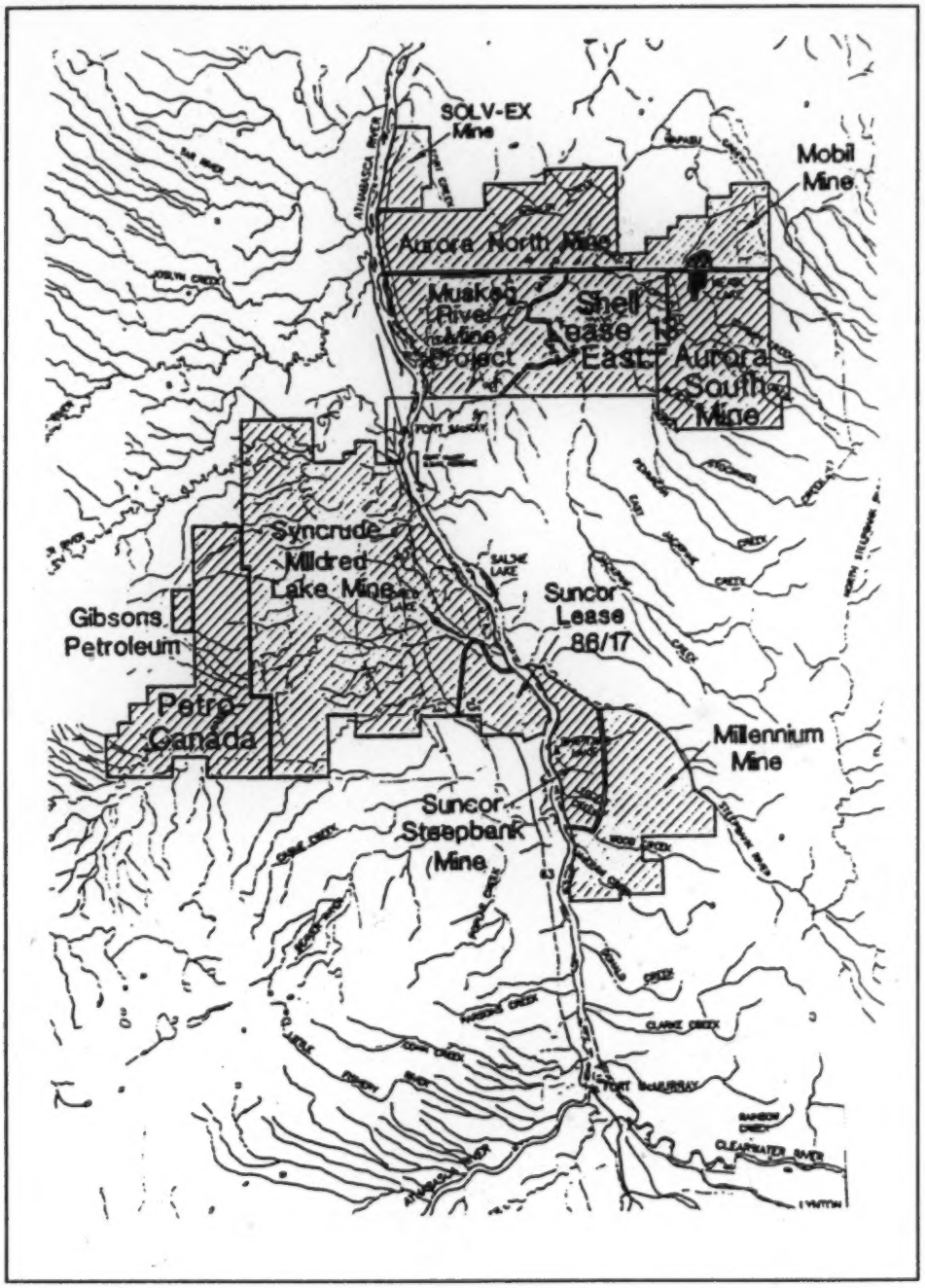


Figure 1.2 Location of Fort McKay in relation to oil sands companies.

In Fort McKay, electric power is provided by Alberta Power and natural gas is provided by Northwest Utilities. Potable water is piped from a water treatment plant within the community to individual homes. Sewage disposal is provided on an individual basis through separate privies, septic tank pumpouts or field systems. Moreover, the community is serviced partially by a municipal sewage system. Garbage pick up is provided weekly by the municipality. There is also a modified landfill, which is adjacent to the community (McKay, 1999).

Fort McKay has an elementary school that is operated by the Northland School Division. It provides education for kindergarten up to grade eight students. Students are then bussed to Fort McMurray to continue their education. There is a Fire Department in the community, which provides ambulance services. Health services are available in Fort McMurray (McKay, 1999).

2.0 Literature Review

2.1 Concept of Exposure Assessment

2.1.1 Approaches to Exposure Assessment

The definition of exposure is when an individual is exposed to a pollutant at a certain concentration and for a specific time period.

$$E_i = \int_{t_1}^{t_2} C_i(t)dt \qquad \textbf{(Eq. 2.1)}$$

where

E_i = exposure to pollutant i (mg)

$C_i(t)$ = concentration of pollutant i, which varies as a function of time (mg/day)

dt = increment of time from t_1 to t_2 (day)

Total Human Exposure (THE) model has been used since the 1980s to determine human exposure to environmental pollutants with known precision and accuracy (Ott, 1990). For this model, the target that is at risk must be identified. If the goal is to protect public health, then the target is people. Then the links for a particular target and the pollutant of concern have to be established. The link is termed a "route of exposure" and it is made up of sources, movement, exposure, dose and effects of the pollutant. The information on all these components must be known before one can characterize the relationship between the source and the effect of a pollutant (Ott, 1990; Lioy, 1990).

A conceptual model of THE is shown in Figure 2.1. There is a bubble around the target, which is a human. The contact of the pollutant with the target is through

air, food, soil and water. Any contact with the pollutant is considered as exposure. The routes of exposure have to be identified. They include inhalation, dermal or ingestion. If there are multiple routes of exposure, THE will define the exposure from all the possible routes of exposure. Thus, THE covers all routes of exposure regardless of the carrier medium (Ott, 1990). Moreover, it considers all the microenvironments (any location or space where the pollutant exposure level can be considered to be relatively homogeneous) that people are in (WHO, 1997; Ott, 1990).

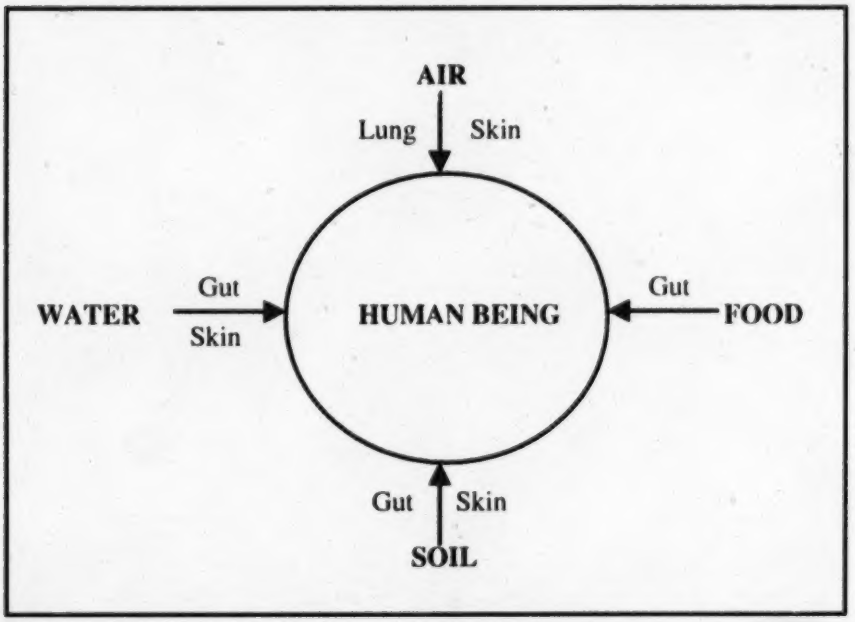


Figure 2.1 Conceptual model of total human exposure (taken from Ott, 1990).

With THE approach, there are two complementary monitoring approaches that have been devised to estimate human exposure- direct and indirect approaches. These approaches are shown in Figure 2.2 (WHO, 1997; Covello and Merknofer, 1993; Ott, 1990). Results of exposure assessment are then used for risk assessment of potential

health effects of the pollutant and for estimation of possible contributions of exposure routes to the risk (WHO, 1997).

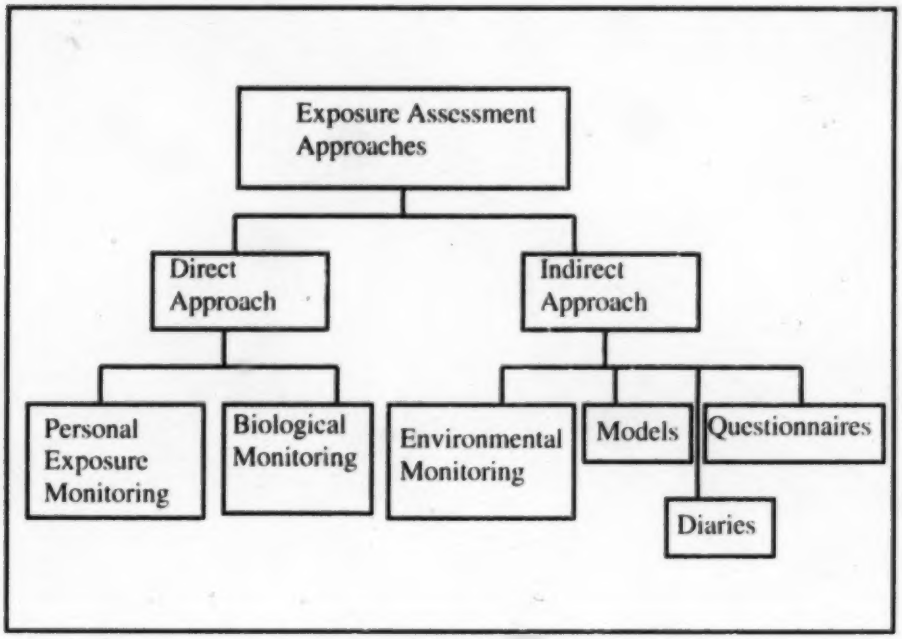


Figure 2.2 Approaches to exposure assessment (adapted from WHO, 1997; Covello and Merknofer, 1993; Ott, 1990).

Direct approaches include both personal exposure monitoring (PEM) and biological monitoring. It can be enhanced by combining both PEM and biological monitoring with time location activity data, which will relate contact, and transfer of a pollutant. Direct approaches to exposure assessment are more representative of an individual's exposure to a pollutant since they measure exposure to a pollutant at a point of contact with the human body (WHO, 1997; Covello and Merknofer, 1993; Ott, 1990).

The second approach to exposure assessment, which was employed in this study, is the indirect approaches. It measures the factors that affect exposure rather than the exposure itself (Covello and Merknofer, 1993). Indirect approaches of exposure assessment include microenvironmental monitoring, modeling, diaries and questionnaires (WHO, 1997; Covello and Merknofer, 1993; Ott, 1990). Fixed-site monitors are also used to measure concentrations of a pollutant in media. With this type of monitoring, the ability to describe spatial and temporal variation of concentrations of a pollutant found in media is often a problem. Thus, selection of a particular site or measurement can have a strong effect on the numerical result. Indirect methods are cheaper and less representative of personal exposure to a pollutant. They can only approximate exposure by averaging the concentrations of a pollutant in the microenvironment (WHO, 1997; Covello and Merknofer, 1993; Ott, 1990).

Strength in exposure monitoring lies in the fact that it provides estimates of individual and population exposures. Also, it helps define the causal connections between sources of a risk agent and resulting levels of exposures to human and other populations. Some limitations of exposure assessment are the great diversity of environmental media and exposure pathways, which makes collecting statistically meaningful samples difficult. Moreover, the constraint of money and time demand that sampling be performed at convenient sites and times. Thus, exposure monitoring often does not provide an unbiased estimate but rather an index. Lastly, the translation of measurements obtained from fixed monitoring stations into actual exposures

experienced by people or animals that move from place to place is another limitation of exposure monitoring (Covello and Merkhofer, 1993).

2.1.2 Exposure and Dose

Dose-response models are used to assess the adverse health effects from exposure to a substance such as SO_2. Exposure to a substance varies over time and the health effects vary with the frequency and severity of the dose. Moreover, a time delay may be experienced between the onset of the adverse health effects and exposure. As shown in Figure 2.3, at a low dose there is no effect regardless of the duration of exposure. At a slightly higher dose, subtle effects may be experienced by a small percentage of the population. At an even higher dose of sufficient duration, nearly all of the population will experience an adverse effect (Covello and Merkhofer, 1993).

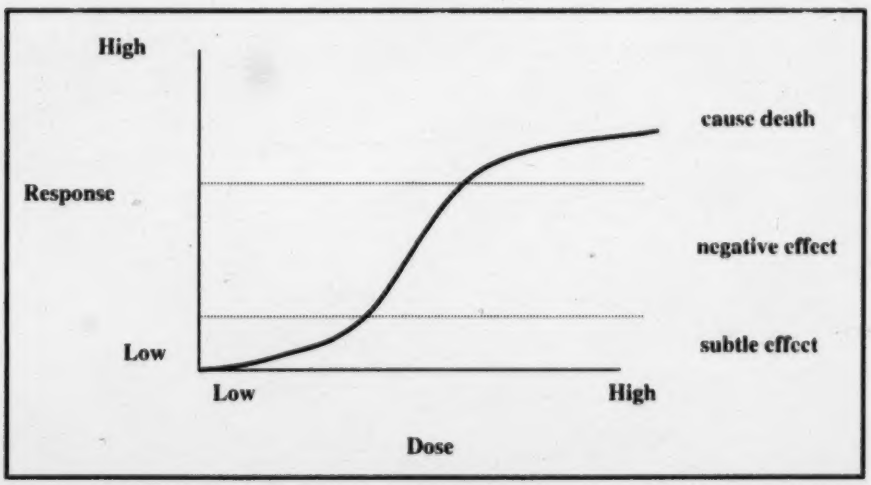


Figure 2.3 General dose-response curve (taken from Covello and Merkhofer, 1993).

The dosage of airborne SO_2 that renders it toxic depends on the duration and concentration of the exposure. Typically dose is expressed as a cumulative exposure or rate per unit time. Thus, at constant dose, it varies inversely with time and proportionally with cumulative exposure or concentration (Covello and Merkhofer, 1993).

2.1.3 Measuring Exposure to Airborne Pollutant

There are many methods to measure exposure to airborne pollutants. However, the measurement technique must be sensitive enough to measure low concentrations. There are three basic strategies: continuous monitors, time-weighted average (TWA) and grab sampling. Figure 2.4 illustrates the differences between these strategies (Yocom and McCarthy, 1991).

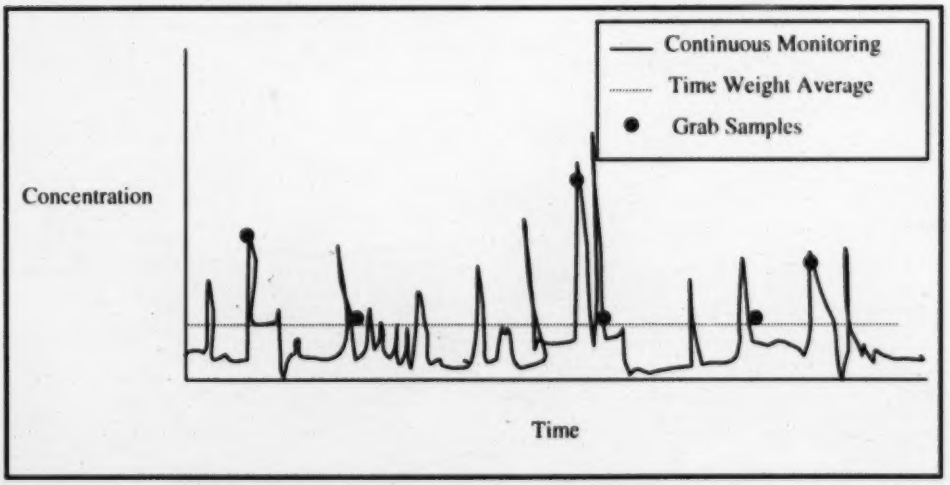


Figure 2.4 Different strategies to measure exposure to airborne pollutants (adapted from Yocom and McCarthy, 1991).

Continuous monitors can measure short-term fluctuations and calculate long term averages. This constitutes real-time monitoring. Monitoring can be done at fixed locations either indoors or outdoors (Yocom and McCarthy, 1991). The second measuring technique is TWA. It represents a sample collected over time and averaged and thus removes the exposure variation components of higher frequency of the data. Few valuable data will be lost if the averaging time is chosen correctly (WHO, 1997). The third measurement technique is grab sampling. Grab sampling is used for single, short-term measurement of indoor air pollutants. This technique will not be suitable if concentrations of the indoor air pollutants are varying rapidly (Yocom and McCarthy, 1991).

2.2 The Contaminant – Sulfur Dioxide

2.2.1 Chemical Characteristics

SO_2 is a colorless gas with a pungent odor. It can be detected by taste or odor by people at concentrations of 1,000-3,000 $\mu g/m^3$ (0.35-1.05 ppm) (WHO, 1979; NIOSH, 1977). It is liquid under pressure and it is readily soluble in water to form sulfurous acid (H_2SO_3) (United States Agency for Toxic Substances & Disease Registry et al., 1998; Maron et al., 1995; WHO, 1979). SO_2 has high vapor pressure, low boiling and melting points. In pure solutions, SO_2 is oxidized slowly to form sulfuric acid (H_2SO_4). In the presence of catalyzing agents such as manganese or iron salts, the oxidation reaction occurs much slowly (WHO, 1979). Table 2.1 lists some of the physical and chemical properties of SO_2 (United States Agency for Toxic Substances & Disease Registry et al., 1998).

Table 2.1 Physical and chemical properties of sulfur dioxide (adapted from United States Agency for Toxic Substances & Disease Registry et al., 1998).

Property	Sulfur Dioxide
Molecular Weight	64.06 g/mol
Color	Colorless
Physical state	Gas at ambient conditions
Melting point	-72.7°C
Boiling point	-10°C
Density	2.927 g/L (gas) or 1.434 g/cm^3 (liquid)
Odor	Strong odor, suffocating
Solubility in water at 0°C	22.8 g/100cc
Solubility in water at 20°C	11.3 g/100cc
Solubility in water at 90°C	0.58 g/100cc
Vapor pressure	330 kPa at 20°C
Flammability limits	Non-flammable

Once SO_2 is released into the atmosphere, it can react with soil, water and air. Soil can absorb SO_2 by diffusion. This absorption is dependent on pH and moisture content of the soil. In the water, SO_2 is very soluble and it can form sulfurous acid. Surface water can receive SO_2 by dry and wet deposition from surface runoff and subsurface drainage and from the atmosphere (United States Agency for Toxic Substances & Disease Registry et al., 1998). In the air, SO_2 may be oxidized to sulfur trioxide (SO_3), H_2SO_4 and other sulfates, for example sodium sulfate, either photochemically or catalytically (United States Agency for Toxic Substances & Disease Registry et al., 1998; Elsom, 1987; WHO, 1979). The reactions involved are either homogeneous-phase reactions (oxidation in gas or liquid phase) or heterogeneous gas-solid reactions (oxidation on the surface of particles). The residence time of SO_2 in the atmosphere is approximately 10 days (United States Agency for Toxic Substances & Disease Registry et al., 1998).

2.2.2 Sources of Sulfur Dioxide

Atmospheric SO_2 is produced from both natural or anthropogenic sources. Natural sources of SO_2 are from volcanic eruptions. The sulfur compounds emitted by volcanoes are mostly SO_2 and H_2S along with smaller amounts of SO_3 and various sulfates (United States Agency for Toxic Substances & Disease Registry et al., 1998; Kellogg et al., 1972). Anthropogenic sources of SO_2 are divided into industrial sources, domestic sources and vehicular sources (WHO, 1979). Industrial sources of SO_2 are produced from combustion of fossil fuels such as coal, and oil burning electric power plants. During oil sands operations, SO_2 is produced from the combustion of coke used to fuel the utility plants and the flaring of waste gas. The emission of SO_2 is related to the sulfur content of the fossil fuels and total amount of fossil fuels that is consumed. Thus, the emission of SO_2 is related to population density of an area (United States Agency for Toxic Substances & Disease Registry et al., 1998; Meyer, 1983). Copper smelters, oil refineries and domestic and industrial heating systems contribute to local sources of SO_2. Since SO_2 is heavier than air, it settles to the ground within a few miles of its source as it enters the sulfur cycle. On the ground, SO_2 oxidizes to sulfate which is a vital component of plant nutrients (Meyer, 1983). Domestic sources of SO_2 include burning soft or hard coal and oil, kerosene and stove oil and light fuel oil (Ritchie and Arnold, 1984; WHO, 1979). Vehicular emission of SO_2 is a result of burning diesel vehicles (WHO, 1979). SO_2 is also found in bleaching agents, pesticides and fungicides, preservatives, disinfectants and antioxidants such as rubber, paints, vegetable oil and prepared foods (Pease, 1999).

2.2.3 Indoor/Outdoor Relationship

Indoor concentrations of SO_2 will be lower than outdoor concentrations due to reactive property of SO_2 with interior surfaces. Indoor absorption of SO_2 is by concrete, brick, tile, unpainted wood, wallpaper, damp emulsion-painted surfaces and dirty metal surfaces (WHO, 1982; Spedding, 1969). Absorption of SO_2 by concrete and cement is due to the porosity of the material. There can also be absorption of SO_2 by plywood, gypsum board and wood pulp based paper (Meyer, 1983; Spedding, 1969). Moreover, locations of moisture indoors such as in damp cracks or patches due to leakage, SO_2 will dissolve in water and oxidize to form sulfate particulates, especially on active particulate surfaces, (Meyer, 1983). SO_2 can speed up the corrosion of metals especially iron, steel, zinc, copper and nickel because it encourages formation of sulfuric acid on the metal surface under moist conditions (Elsom, 1987; Spedding, 1969). The indoor reduction of SO_2 concentrations is also due to its absorption onto waxed floors and fabrics such as carpets, furniture, bed clothing and curtains. No detectable absorption of SO_2 is seen on surfaces that are gloss-painted, clean metal or treated wood surfaces or were coated with dry emulsion paint (Spedding, 1969; Walsh et al., 1977).

Outdoor levels of SO_2 are highest in the winter. This high level is a result of the increased burning of fossil fuel in the winter to provide heat and reduced reactivity of SO_2 under colder temperatures. In addition, during winter the more stable air mass will result in the long range transport of the higher concentrations of SO_2 to greater distances (Golder Associates and Concor Pacific Environmental Technologies, 1998). Moreover, in winter, meteorological conditions are characterized by light wind and

below freezing temperatures. Temperature inversion occurs where the ground is cooler and the temperature is warmer as the altitude increases to the upper atmosphere. Thus, this inversion results in a layer of stagnant cold air near the ground which will trap air pollutants emitted at low level sources (Elsom, 1987). Furthermore, removal rate of SO_2 due to deposition is lower as a result of reduced vegetative activities (Golder Associates and Concor Pacific Environmental Technologies, 1998).

2.2.4 Health Effects of Sulfur Dioxide

SO_2 is considered one of the criteria pollutants in the United States (Pease, 1999). Table 2.2 lists Alberta and Canadian air quality guidelines for SO_2. The acceptable Alberta guideline for 1 hour, 24 hour and annual concentration of SO_2 in the air is 450 $\mu g/m^3$, 150 $\mu g/m^3$ and 30 $\mu g/m^3$ respectively. These guidelines are intended to provide adequate protection against acute and chronic exposures to SO_2 (Golder Associates and Conor Pacific Environmental Technologies 1998).

Table 2.2 Federal and Alberta Air Quality Guidelines for sulfur dioxide (adapted from Golder Associates and Conor Pacific Environmental Technologies, 1998).

		Federal Objectives		
Duration	**Alberta Guidelines ($\mu g/m^3$)**	**Desirable ($\mu g/m^3$)**	**Acceptable ($\mu g/m^3$)**	**Tolerable ($\mu g/m^3$)**
Annual	30	30	60	N/A
24-hour	150	150	300	800
1-hour	450	450	900	N/A

N/A = Not Available

The major route of exposure to SO_2 is through inhalation. A secondary route of exposure is dermal. Once SO_2 enters the body, it breaks down into sulfate and leaves through the urine. SO_2 is highly irritating to the skin, eyes and mucous

membranes (United States Agency for Toxic Substances & Disease Registry et al., 1998; Maron et al., 1995; Anahem Inc. et al., 1982). Some of the symptoms of SO_2 exposure include coughing, sputum production, difficulty breathing and burning of the nose, and throat tract (United States Agency for Toxic Substances & Disease Registry et al., 1998; WHO, 1979).

Table 2.3 Symptoms of SO_2 exposure (adapted from WHO, 1979).

Concentration ($\mu g/m^3$)	Length of exposure (min)	Effects
2,900- 2,300	10	• Increased pulse rate • Decreased tidal volume • Increased respiratory rate
2,900	10-30	• Increased pulmonary resistance
2,500	15	• Increased respiratory resistance
2,000	60- 180	• Decreased nasal mucous flow • Decreased cross-section of nasal passage
1,100	120	• No effect on pulmonary function through exposure

Some of the symptoms of SO_2 exposure as a function of time and concentration of SO_2 are summarized in Table 2.3. SO_2 causes distress at a concentration above 2,100 $\mu g/m^3$. At concentration below 1,100 $\mu g/m^3$, it is not noticed by most people (WHO, 1979). Individuals that are more susceptible to SO_2 exposure include exercising asthmatics, asthmatics both adult and children, the elderly with pre-existing respiratory or vascular problems, workers and non-asthmatics sensitive to cold (United States Agency for Toxic Substances & Disease Registry et al., 1998; Goldstein and Weinstein, 1986; WHO, 1979). Long term exposure causes lung edema, lung tissue

damage and sloughing off of the cells lining the respiratory tract (United States Agency for Toxic Substances & Disease Registry et al., 1998; American Thoracic Society 1996; WHO, 1979). Moreover, long term exposure increases the risk of chronic respiratory disease (Wood Buffalo Environmental Association, 1998).

2.2.5 Vegetative Effects of Sulfur Dioxide

SO_2 can be removed from the air by direct uptake by plant leaves. Excessive quantities of airborne SO_2 can have profound effects on vegetation. Acute injury to plants as a result of SO_2 exposure includes bleached patches on broad-leaved plants or bleached necrotic streaking on either side of the mid-vein parallel veined leaves (Elsom, 1987). Long-term SO_2 exposure includes bleaching of the chlorophyll to give a mild chlorosis or discoloration of the leaf. Thus, SO_2 exposure interferes with the photosynthesis action of the plants, causing a reduction in growth and yield of the plants. Plants that are more susceptible to SO_2 exposure include alfalfa, barley, cotton, lettuce, lucerne, rhubarb, spinach and sweet pea. Lichen is especially sensitive to SO_2 exposure because it contains relatively small amount of chlorophyll. But SO_2 exposure is not always damaging to plants. In some SO_2 deficient areas, vegetative exposure to SO_2 may be beneficial. However, after some time, SO_2 may decrease the pH of the soil and thus requiring the addition of lime (Gunn et al., 1995; Elsom 1987).

2.3 Methods of Sampling Sulfur Dioxide

Measurement of SO_2 in air has traditionally been performed through active sampling methods. The operational principle of active samplers is that the desired

analyte is measured by using a pump to pull a known volume of air through a filter that has been treated with a gas specific reactant (Greyson, 1990; Alberta Health, 1997). The sample volume is equal to the flow rate multiple by the time (Coulson, 1981). After exposure, the filter is processed in the lab to determine the mass of analyte that is collected (Greyson, 1990; Alberta Health, 1997). Typical active sampling methods for measuring SO_2 in the atmosphere include the pulsed fluorescence method, the West-Gaeke method and the annular denuder system (Leaderer et al., 1994; Lee et al., 1993; Lodge et al., 1989; EPA, 1982; Reiszner and West 1973).

2.4 Previous Studies of Sulfur Dioxide

A number of previous studies have investigated the relationship of SO_2 in indoor and outdoor air. One of the earlier studies was conducted in 65 Rotterdam homes, where it was found that indoor levels of SO_2 were consistently lower than outdoor levels by 51%. It was also noted that age of the home influences the indoor levels and newer houses with fresher plaster had lower levels of SO_2. Moreover, the indoor concentration of SO_2 may have resulted from faulty flues in heaters (Biersteker et al., 1965). Spengler et al. (1979) studied indoor and outdoor levels of SO_2 in six American cities and reported that indoor levels ranged from 1 to 22 $\mu g/m^3$ and outdoor levels ranged from 5 to 52 $\mu g/m^3$. Also, the outdoor levels were 50-70% more than the indoor levels (Spengler et al., 1979). SO_2 was also measured during winter (March) and summer (July-August) months in Boston to determine the indoor infiltration of SO_2 from outdoors. These findings were consistent with previous

investigations of SO_2 where the indoor levels (winter: 1.0 $\mu g/m^3$; summer: 3.8 $\mu g/m^3$)were lower than the outdoor levels (winter: 12 $\mu g/m^3$; summer: 9.1 $\mu g/m^3$) for both seasons. It was also reported that lower air exchange rates of houses would affect the indoor concentrations of SO_2 by increasing the indoor residence time of the pollutant. This will cause the removal of SO_2 by gas collisions with indoor surfaces resulting in a decreased indoor level of SO_2 (Brauer et al., 1991; Koutrakis et al., 1991). SO_2 was continuously monitored indoors and outdoors at two sub-divisions in Houston, Texas by a mobile van (Stock et al., 1985). These investigations also found that outdoor levels of SO_2 were 50% more than indoor levels. Investigations of the indoor and outdoor levels of SO_2 were also conducted in summer and winter in Taipei (Chan et al., 1994). Summer samples were taken at 12-hour intervals and in the winter, samples were taken at 24-hour intervals. The mean outdoor level of SO_2 in the summer and winter was 20 $\mu g/m^3$ and 22 $\mu g/m^3$ respectively. The mean indoor level of SO_2 in the summer and winter was 6.5 $\mu g/m^3$ and 6.3 $\mu g/m^3$ respectively. It was shown that the outdoor levels of SO_2 were two to three times higher than the indoor levels. Factor contributing to the higher outdoor level of SO_2 was reported to be the increased number of vehicles on the road (Chan et al., 1994). An investigation was also conducted on main roads of Tokyo and in residential areas of Beijing (Ando et al., 1996). It was found that the concentrations of SO_2 were five times higher in the residential area because of the use of coal and coal gas as indoor sources of fuel (Ando et al., 1996). A more recent study was conducted in Korea where sampling was done during the summer months of July to August 1995 (Lee et al., 1997). The results also indicated that the mean indoor levels of SO_2 (6.2 $\mu g/m^3$) were lower than the mean

outdoor levels (11 $\mu g/m^3$). Moreover, indoor penetration of SO_2 was low which suggests that deposition of SO_2 on surfaces indoor lead to its reduced concentration indoors. A correlation between the indoor levels of SO_2, outdoor levels of SO_2 and air exchange rate were found (Lee et al., 1997).

Studies were also conducted from October 1985 to March 1986 in Saskatchewan and Ontario to compare the outdoor rural and urban SO_2 concentrations as a result of long range transport of the air pollutant from industrial sites (Stern et al., 1994). It was found that in five rural communities in Saskatchewan, the mean outdoor SO_2 concentration was 1.1 $\mu g/m^3$. The SO_2 concentration in 5 urban communities located in southwestern Ontario averaged 5.5 $\mu g/m^3$. Thus, the concentration of SO_2 was lower in rural communities (Stern et al., 1994). This finding is confirmed by Altshuller (1984), which found that in a rural site in St. Louis, the outdoor SO_2 concentrations averaged 28 $\mu g/m^3$ in the year 1976. The concentrations of SO_2 from July 1975 to March 1977 in an urban industrial area in St. Louis averaged 42 $\mu g/m^3$. In addition, the concentrations of SO_2 from July 1975 to March 1976 in an urban residential area in St. Louis averaged 33 $\mu g/m^3$. Thus, the level of SO_2 was lower in the rural area compared to both urban industrial area and urban residential area (Altshuller 1984). A study of indoor and outdoor levels of SO_2 was conducted in four urban Canadian cities over a 5-year sampling period in 1988 to 1992 (reported in Hrudey and Kindzierski, 1998). The mean outdoor levels were 8 $\mu g/m^3$ for Edmonton, 11 $\mu g/m^3$ for Vancouver, 14 $\mu g/m^3$ for Toronto and 16 $\mu g/m^3$ for Montreal. These outdoor levels were higher than reported outdoor levels of SO_2 (0.8 –1.6 $\mu g/m^3$) at a rural community located between Edmonton and Sherwood Park (Hrudey and

Kindzierski, 1998). But the mean outdoor concentrations of SO_2 in these urban centers were low in comparison to levels of SO_2 in a rural community in southern Ontario, which averaged 19 $\mu g/m^3$. This is a result of the location of the community, which is downwind from industrial sources in Ontario. Moreover, strong winds lead to a more rapid transport of the pollutant to greater distances (Daum et al., 1989). Kindzierski and Sembaluk (1998) also measured indoor and outdoor concentrations of SO_2 in late fall for five weeks in the urban center of Sherwood Park and the rural community of Boyle, Alberta. It was found that the rural community of Boyle (indoor: 0.5 $\mu g/m^3$; outdoor: 4.3 $\mu g/m^3$) had consistently lower concentrations of SO_2 both indoors and outdoors compared to the urban center of Sherwood Park (indoor: 1.4 $\mu g/m^3$; outdoor: 9.9 $\mu g/m^3$). The higher concentrations of SO_2 in Sherwood Park was reported to be a result of increased vehicular activities and increased industrial emissions in the urban area (Kindzierski and Sembaluk, 1998).

3.0 SO_2 Sample Design, Collection and Analysis

3.1 Statistical Design

3.1.1 Sampling Plan

3.1.1.1 Sampling Frame

The population studied consisted of 129 single-family residences, which is made up of both houses and trailers in the community of Fort McKay. The Fort McKay Industrial Relations Corporations provided a list of all the residences in Fort McKay. The list gave a map reference as shown in Figure 3.1. Moreover, the resident's name and housing type of each unit were also provided. Initially, one of the field staff was sent to verify the information of the homes on the list. There was a small cluster of Metis housing in the south end of the community. The field staff were sent to determine the housing type and the housing number for each of the Metis dwellings. All of the information was combined into a final list. Based on the list, it was found that the community consisted of 89 houses, 40 trailers, 1 duplex and 1 threeplex. The multiple family residences were excluded, therefore the sample size was taken as 129 households. Due to the small size of the community, it was decided to recruit 30 households to participate in the study.

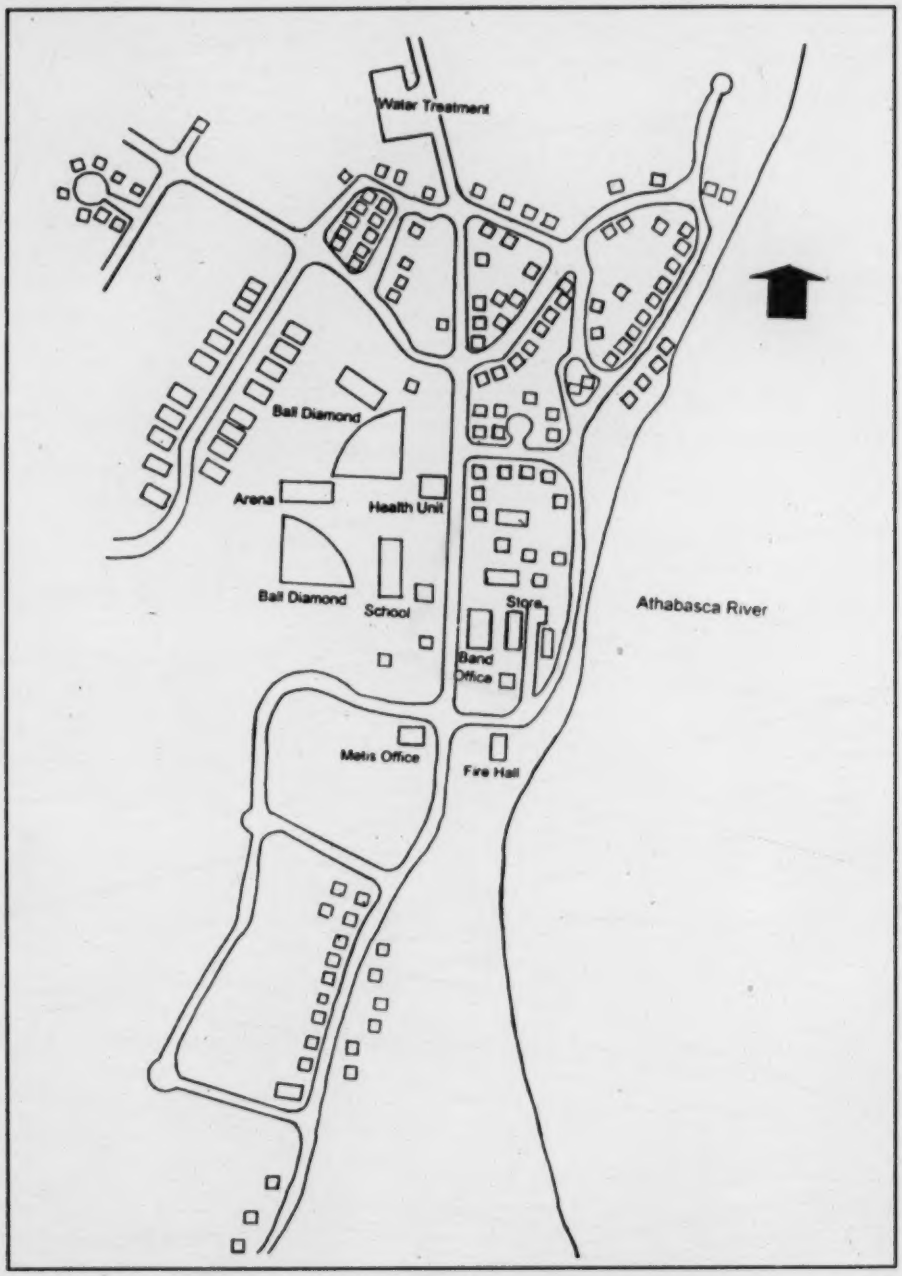


Figure 3.1 Layout of the community of Fort McKay.

3.1.1.2 Sampling Techniques

It is rare to collect data on all the subjects in a particular study. Thus, a sample provides a practical and efficient means to collect the data and it serves as a representation of the population (Henry, 1990). There are a few sampling methods that can be used such as probability sampling, simple random sampling, cluster sampling, systematic sampling and multistage sampling (Satin and Shastry, 1993; Henry, 1990; Cox et al., 1988; Stuart, 1984).

Probability sampling is selecting members of a population randomly. One can use random devices such as a table of random numbers to determine which units in the populations are to be included. These random devices eliminate subjective bias in the selection process and underlie the theories used to infer the sample results to the population (Henry, 1990). Simple random sampling is listing the families of a community by a number and then picking numbers randomly until the desired numbers of sampling units are reached. Each member of the community has an equal probability of being selected. Stratified sampling is dividing the population into subgroups or stratum, either geographical or socio-economical. Samples are then randomly selected from each strata either using probability sampling or simple random sampling. Cluster sampling involves random sample groups or clusters of adjacent units in the population. Clusters are families within the same area of the city or block. This type of sampling is time saving and less expensive because it requires less traveling time. However, it has large error and is less precise because adjacent sampling units tend to have similar characteristics. Systematic sampling is accomplished by listing the sampling units in order and then selecting the members of

population at equal intervals. Multi-stage sampling is sampling of the subgroup within the sampling clusters. The advantage is that the researcher can concentrate on a smaller number of areas with a reduction in required staff and money. Also, researchers need only the sampling units listing rather than a complete list of the population demographics (Satin and Shastry, 1993; Henry, 1990; Cox et al., 1988; Stuart, 1984).

One problem of any type of sampling is the level of non-response. Non-response contributes to the magnitude of the sampling bias produced from sampling. If non-response is truly random, then it does not represent a bias. But usually this is not the case because most frequently non-respondents come from a definable subgroup of the population. Non-response can be minimized by multiple callbacks, non-response follow-up or monetary incentives (Henry, 1990; Cox et al., 1988).

The sampling technique used in the study was stratified sampling. The population was divided into two stratas: houses and trailers. Stratified sampling minimizes variance and increases the precision of sampling because the environmental condition within these strata is more homogeneous than for the population as a whole. Also, nearly half of the trailers were located in a cluster on the west side of the community. Thus, stratification by housing type helped to ensure a geographically representative sample. No reasonable assumptions about the variance within each stratum could be concluded, so the sample size was allocated proportionally. Based on the community's information, the proportion of houses and trailers were 69% and 31%, respectively. Hence, according to the sample size of 30 households, the number of houses and the trailers in the two stratas were 21 houses and 9 trailers.

3.1.1.3 Sample Selection Procedure

The houses in Fort McKay were listed sequentially by housing unit number and the list was numbered from 1 to 89. Two-digit random numbers (00-99) were generated by selecting two columns of numbers from a table of random numbers. The numbers 00 and 99 were discarded. A house corresponding to a selected random number was recorded on the sampling list. If the same number was selected again, it was discarded. Such a selection process is random selection without replacement. The process was repeated until 21 houses were selected. The trailers were also listed sequentially by housing unit number and the list was numbered 1 to 40. The same trailers were listed again by housing numbers and the list was numbered 41 to 80. The trailers were listed twice because the random number table was from 00 to 99. Random numbers were generated using the random number table of 00 to 99 and the corresponding trailers were selected. The numbers 00 and 81 to 99 were discarded. This was repeated until 9 trailers were chosen.

This random list of 30 units (21 houses and 9 trailers) was initially given to the field staff. Out of the 30 houses, 16 houses agreed to participate. An additional list of 12 randomly chosen houses was given to the field staff as a result of non-response. Out of the 12 randomly chosen houses, three agreed to participate. Thus, out of a list of 42 randomly chosen houses, 19 houses agreed to participate. The response rate was 45%. One additional house volunteered, giving a total of 20 participating houses. As for the trailers, a list of 18 randomly chosen trailers was sent to the field staff. Ten trailers agreed to participate. The response rate was 56%. Due the nature of the

community and non-response, 20 houses and 10 trailers were selected as opposed to the ideal sample proportion of 21 houses and 9 trailers.

3.1.1.4 Field Recruitment Procedure

The Fort McKay Industrial Relations Corporation sent out an initial information letter about the study to the community of Fort McKay. After the randomly generated list of 42 houses and 18 trailers was given to the field staff, they tried to recruit the households for the study using a door to door campaign strategy. On the first visit, the field staffs were instructed to explain the study and attempt to gain agreement to participate in the study. A participant information sheet was given to the household. It briefly explained the purpose of the study and what would be done at each of the drop-off and pick up visits and what would be required of the participant (including the amount of their time, use of their home and the completion of a questionnaire). The field staff were then required to fill in the recruitment status form. If the household agreed to participate, the participant was required to sign the recruit consent form and indicate a date and time within the sampling schedule that they would be available. The recruitment package is shown in Appendix A. A sampling reminder was given to the households a few days before the initial visits. If the home was vacant or the residents refused to participate in the study, their homes were taken off the list. In instances when no one was home, these homes were re-visited a number of times until they were regarded as non-response. The recruitment procedure continued until the appropriate number of houses and trailers were chosen.

3.2 Questionnaire

Questionnaires are indirect methods to assess human exposure. The objective of the questionnaire is to identify household characteristics and activities, which will characterizes the indoor and outdoor sources of SO_2. For this study, three questionnaires were developed. The first questionnaire, *Household Characteristics*, was designed to identify household characteristics. Questions included asking the ages of homes and heating and ventilation systems, type of fuel, number of habitants and the characteristics of the attached structures such as garages. An example of the questionnaire is provided in Appendix B. In order to elicit satisfactory responses, the responses to the questions were in a "Yes" or "No" format. However, spaces were provided for comments in case individuals felt that a yes or no answer was not sufficient. Field staff that were residents of the community administered the questionnaires.

The second questionnaire, *Personal Exposure and Activity Questionnaire* identified potential sources of SO_2 in the homes. Household sources such as the opening and closing of windows and carpet cleaning were identified. This was followed by questions identifying specific activities such as smoking, hobbies and renovation. An example of the questionnaire is provided in Appendix B.

The third questionnaire, *Household Activity*, was a follow-up to questionnaire one and two. The first section was a repeat of questionnaire two and the second section identified any additional activities that were performed. An example of the questionnaire is provided in Appendix B.

The three questionnaires served as helpful sources of information for the identification of any abnormalities in the data.

3.3 Time Activity Diaries

Indoor and outdoor air pollution can vary from location to location. Actual exposure of an individual to a pollutant varies greatly because of the amount of time that people spend in the different microenvironments. Therefore, to characterize human exposure to air pollution, time activity surveys can be used to find out where people spend their time and the activities they engage in. The general approach to determine the activity patterns of an individual is through the use of a diary where individuals write down what their activities are and the duration of the activities. Other methods are the interviewing technique where individuals try to recall their activities and the direct observation of the participant (Leech et al., 1996; Lioy, 1995; WHO, 1982).

The microenvironments where people spend their time can be divided into five categories– indoors at home, indoors at work or school, indoors at restaurants, bars or other public establishments, outdoor and in an operating motor vehicle (or near a roadway) (Hrudey and Kindzierski, 1998). Figure 3.2 illustrates the amount of time spent in each of the microenvironment by individuals aged 12 years or older in Canada and in United States. Figure 3.3 illustrates the amount of time spent in each of the microenvironment by individuals aged 11 or younger in Canada and between 5 and 12 years of age in United States.

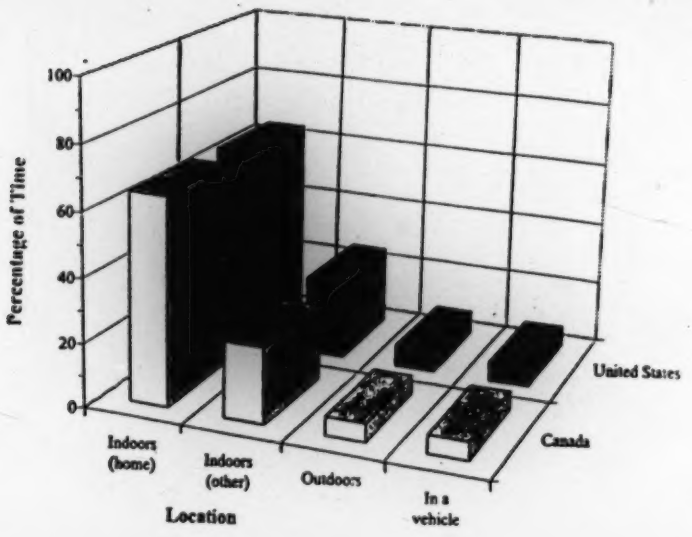


Figure 3.2 Average amount of time spent at various locations by people aged 12 years or older in Canada and United States (taken from Hrudey and Kindzierski, 1998).

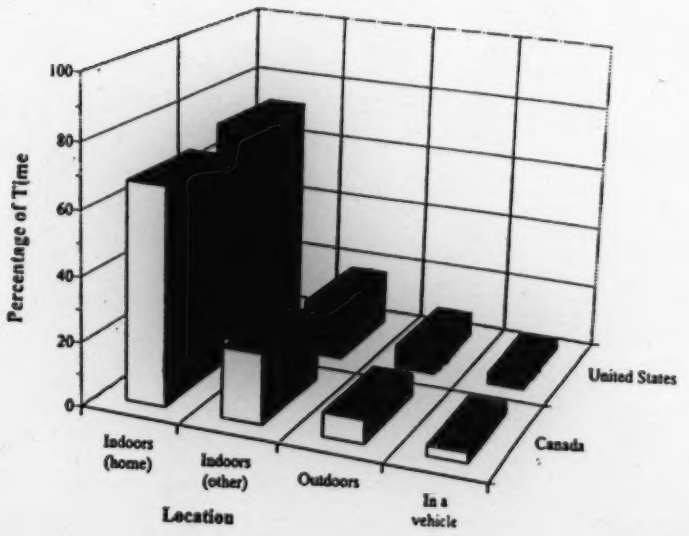


Figure 3.3 Average amount of time spent at various locations by children aged 11 years and younger in Canada and between 5 and 12 years old in United States (taken from Hrudey and Kindzierski, 1998).

As illustrated in Figure 3.2, the greatest portions of time spent by both Canadians and Americans adults are indoors. On average, they spend approximately 60% of their time indoors at home and 20% of their time indoors at work. The indoor environment is also where most of the children spend most of their time. The average amount of time spent for both Canadian and American children are 72% and 68%, respectively (Hrudey and Kindzierski, 1998; Leech et al., 1996).

The participants in Fort McKay were asked to fill in a 24-hour time-activity diary to identify the general activities and duration of these activities in order to characterize their personal exposure to SO_2. Unfortunately, due to the nature of the information that was needed for the time activity diaries, only a few participants agreed to give the information. From the few completed time activity diaries, it was observed that these participants spend most of their time indoors either at home or at work. This finding is comparable to the study conducted by Leech et al. (1996). Moreover, since SO_2 is mainly an outdoor pollutant, their indoor exposure to it is minimal.

3.4 Passive Sampling

3.4.1 Principle of Passive Sampler

Passive sampling is taking samples of gas or vapor pollutants from the atmosphere at a rate that is controlled by the process of diffusion through a static layer or permeation through a membrane. It relies upon a concentration gradient across a diffusion barrier to result in the mass transfer of gaseous molecules across this barrier (Makkonen and Juntto, 1997; Tang et al., 1997; Coulson, 1981; Martin, 1981). Gas or

vapor molecules enter the diffusion zone and move to the inside of the sampler by molecular diffusion and are absorbed by a collector (Hori and Tanaka, 1996). The collector can be either a solid sorbent in a solution or in a liquid (Coulson, 1981). The principle of operation is based on Fick's first law of diffusion as shown in Equation 3.1 (Makkonen and Juntto, 1997; Tang et al., 1997; Coulson, 1981):

$$J = -D * A \frac{dc}{dx} \qquad \textbf{(Eq. 3.1)}$$

where

J	=	diffusion transfer rate (g)
D	=	diffusion coefficient (cm^2/sec)
A	=	effective cross-sectional area (cm^2)
x	=	distance along the diffusion path (cm)
c	=	analyte concentration at distance x (g/m^3)

The negative sign is due to the decrease of analyte concentration in the direction of diffusion. Equation 3.1 can be simplified as follows (Tang et al., 1997):

$$Q = SR * TWA * t \qquad \textbf{(Eq 3.2)}$$

where

Q	=	mass uptake rate (mg)
SR	=	sampling rate (m^3/min)
TWA	=	concentration of the air pollutant (mg/m^3)
t	=	sampling time (min)

Sampling rate can be determined using Equation 3.3 (Hori and Tanaka, 1996; Coulson, 1981).

$$SR = \frac{(D * A)}{L} \qquad \textbf{(Eq. 3.3)}$$

where

SR	=	sampling rate (cm^3/min)
D	=	diffusion coefficient (cm^2/sec)
A	=	surface area of the sampler (cm^2)
L	=	diffusional length (cm)

For a given contaminant, the sampling rate is dependent on the A/L ratio. As shown in Figure 3.4, varying A/L can change the sensitivity and range of sampling rate. In order to measure low dose levels more accurately, sampling rate can be increased to $(A/L)_3$ ratio , or to measure high exposure levels more confidently, sampling rate can be decreased to $(A/L)_1$ ratio (Lautenberger et al., 1981).

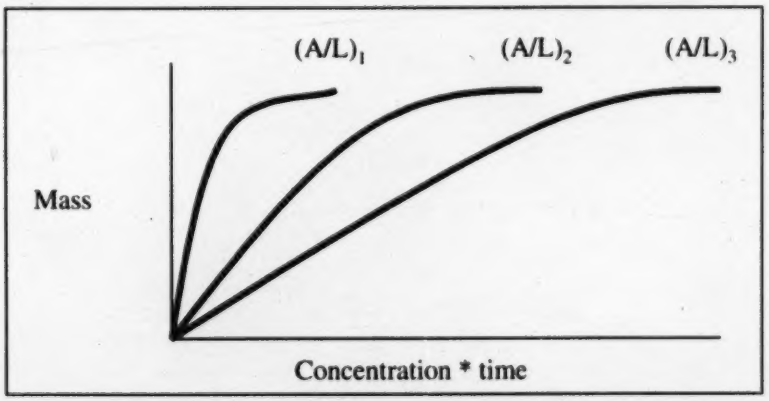


Figure 3.4 Relationship of the area to length ratio of passive monitor to the mass of the analyte collected by increasing the sampling rate from $(A/L)_1$ ratio to $(A/L)_3$ ratio (adapted from Lautenberger et al., 1981).

Another parameter that affects the sampling rate is the diffusion coefficient. The diffusion coefficient is a function of the absolute temperature (Tang et al., 1997; Hori and Tanaka, 1996; Brown, 1993; Coulson, 1981). The most extensive summary of diffusion coefficients of substances in air is provided by Lugg (1968). In addition, surface area of the sampler can also affect the sampling rate of passive samplers. An increase in the surface area of the sample will result in an increased sampling rate. But there are some practical decisions that have to be considered so that the sampler does not become very large (Moore, 1987). Some of the meteorological parameters can also affect sampling rate such as relative humidity and wind speed. Increased relative humidity and decreased wind speed can decrease the concentration of the contaminant that is collected by the passive sampler (Tang et al., 1997; Hori and Tanaka, 1996; Coulson, 1981).

3.4.2 SO_2 Passive Sampler

The passive sampler used in this study was adapted from the design by Leaderer et al. (1994). The original passive sampler design by Leaderer et al. (1994) has a surface area of 9.75 cm^3 with a sampling rate of 41.1 mL/min (Leaderer et al., 1994). When the passive sampler was tested in the Center of Toxicology, it posed a problem if it was used in the Fort McKay study (Gagner, 1998; Alberta Health, 1997). It was because the original sampler has sensitivities of about 92 $\mu g/m^3$ (35 ppb) over a 24-hour sampling period. However, it was noted that the typical concentrations of SO_2 in the Fort McKay area and the Fort McMurray area were between 13 and 26 $\mu g/m^3$ (5 and 10 ppb), respectively (Alberta Health, 1997). The Science Team from the Center

of Toxicology in Calgary concluded that the basic design of the passive sampler by Leaderer et al. (1994) was acceptable. But there had to be some minor changes in order to increase the collection efficiency of SO_2 on the sampler if it were to be used in the Fort McKay study. These changes included increasing the sorbent pad area and decreasing the diffusional length between the sorbent pad and the diffusion membrane (Alberta Health, 1997). The sampler is shown in side view in Figure 3.5.

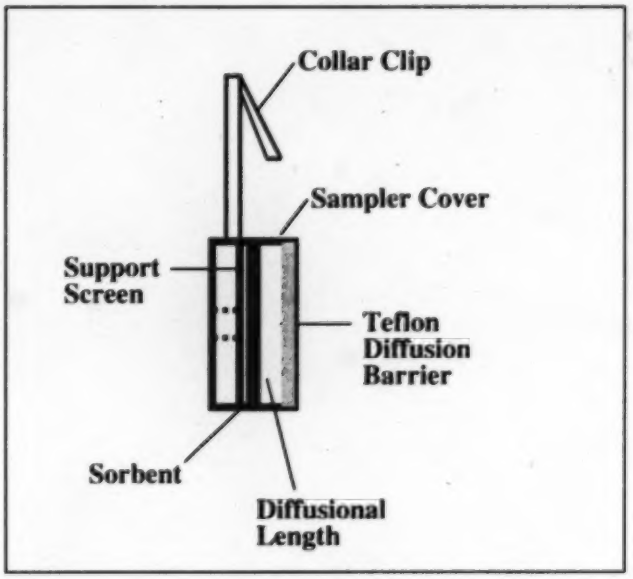


Figure 3.5 Side view of the SO_2 passive sampler (adapted from Gagner, 1996b).

The sampler is a clear light-weight plastic holder with a diameter of 55 mm. It is constructed from a modified 55-Plus Millipore Filter Holder with a removable Teflon diffusion barrier. The diffusion barrier protects the sorbent pad from wind and rain. The sorbent pad area was increased in size from the original design by Leaderer et al. (1994) of 9.75 cm^2 to 23.75 cm^2. The sorbent pad was cleaned in a dry clean air hood and treated with sodium or potassium carbonate. It was loaded into the holder

under zero-air conditions in the Foothills Hospital in Calgary. It should be noted that the sorbent pads were handled with forceps at all times. A specially designed Teflon ring was used to hold the filters in place and a standard bull-dog (collar) clip was used to attach the sampler to various indoor and outdoor stands. After assembly of the samplers, they were placed in polyethylene lids and sealed with parafilm (Alberta Health, 1997).

After the exposed samplers were retrieved from various locations, they were sent to the Center of Toxicology Laboratory in Calgary to determine the mass of SO_2 on the samplers. But before the mass of SO_2 could be determined, the sampling rate had to be known. Since the surface area of the sampler was increased and the diffusional length of the sampler was decreased, the result was an increase in the sampling rate of the passive sampler from the original sampling rate of 41.1 mL/min (Leaderer et al., 1994). From exposure chamber study, the sampling rate was determined in the laboratory by exposing the passive sampler to known concentrations of contaminant for known periods of time and measuring the mass of the contaminant that was collected. The sampling rate was then established as 218 mL/min (Alberta Health, 1997).

To determine the concentration of SO_2 in the atmosphere, it has been known for years that sodium or potassium carbonate can collect the SO_2 from the atmosphere by oxidizing it to sulfur trioxide (SO_3). The treated filters were then processed in the laboratory with hydrogen peroxide, which oxidizes SO_3 to sulfate (SO_4^{2-}). The laboratory reports the mass as "mass of SO_4^{2-} per sampler". The stoichiometry is a

consistent 1:1:1 relationship between SO_2, SO_3 and SO_4^{2-} (Alberta Health, 1997; Gagner, 1996a).

The SO_2 samplers were placed on sampler stands made with PVC materials. The stands were provided by Alberta Health. Both indoor and outdoor stands were 0.9 m in height, which represented the breathing zone of individuals when seated. The outdoor stands had galvanized rain caps to protect the samplers from rain or snow. Also, the legs of the outdoor sampler stands were pegged or weighted down with sand bags to prevent them from toppling over. A diagram of the stand is shown in Figure 3.6.

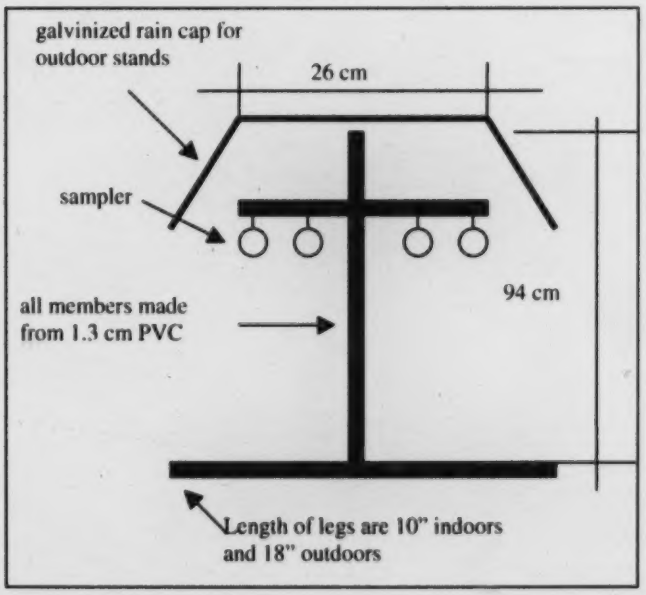


Figure 3.6 Diagrammatic layout of sampler stands provided by Alberta Health.

3.4.3 Advantages and Disadvantages of Passive Samplers

There are two basic types of personal samplers – passive and active. Most of the emphasis has been on active sampling where the sample is collected by drawing air through a sampling device by means of a sampling pump. But since the 1980s, passive sampling has been gaining more notoriety. Passive sampling does not involve a variety of collection devices such as sorbent tubes and bag samplers. It does not need a sampling pump and this equates to fewer calibration and maintenance problems (Rose and Perkins, 1982; Coulson, 1981). Moreover, they are very quiet since there is no sampling pump. Passive samplers have no electrical requirement and thus, they can be used in remote places or rural communities where there is no electricity (Ferm and Svanberg, 1998; Keywood et al., 1998; Coulson, 1981). Passive samplers are lightweight, small and unobstructive. Therefore, they cause no inconvenience for individuals. They are easy to operate since it only involves taking the sampler out of a container. Moreover, they can be used to obtain measurements in large populations simultaneously for epidemiological studies and thus are cheaper for extensive use than active sampling (Leaderer et al., 1994; Auffarth, 1987; Meyer, 1987; Squirrel, 1987; Bartley et al., 1983). Passive samplers can be mailed to the desired locations before and after sampling and they can be stored for periods up to several weeks (Krochmal and Kalina, 1997). The only thing that is required is a reliable timepiece to measure exposure duration (Rose and Perkins, 1982).

The disadvantage of passive samplers is that they measure average concentrations with continual exposure but they cannot measure short-term peaks or variability (Keywood, 1998; Auffarth, 1987). The passive sampler is said to be more

reliable than the active sampler, since it does not experience pump failure. However, the passive sampler does appear to suffer from occasional wild results. Pump failure in the active samplers can be detected, but wild results in a passive sampler cannot be detected. Another disadvantage of the passive sampler is that the sample volume is not known, it is only estimated from laboratory results of uptake rates (Coker, 1987). Passive samplers can only measure gases and vapors. They are not suitable to measure particulates because the diffusion coefficient of particulates in air is several orders of magnitude smaller than gases (Brown, 1993). Lastly, a decrease in air face velocity, which causes stagnant air around the face of the sampler, can cause a decrease in the amount of pollutant that can be collected by the sampler. This effect is explained further in Section 3.4.4.

3.4.4 Sources of Sampling Bias

There are many sources of errors of passive samplers. Insufficient or high wind face velocity can alter physical parameters of passive monitors such as diffusional length and surface area, which can contribute to sources of sampling error. Diffusion coefficients are another source of error in the sampling rate (Makkonen and Juntto, 1997; Rose and Perkins, 1982; Lautenberger et al., 1981). Sensitivities of analytical equipment to contamination and sensitivities of the passive sampler to concentration fluctuations is another form of measurement error. Moreover, determination of a mass of a pollutant on a sampler using Equation 3.2 is another form of measurement error (Alberta Health, 1997; Gagner, 1996a). Lastly, over-sampling can also contribute to sampling error (Cassinelli et al., 1987; Martin, 1981).

The effect of decreased air velocity perpendicular to the face of the sampler results in a decreased sampling rate. The sampling rate is dependent on air movement. When the face velocity is zero, an air pollutant concentration boundary layer is formed on the passive sampler's diffusion barrier surface. The boundary layer is well formed and it results in an increase in the diffusional length and a subsequent decrease in the sampling rate. This phenomenon is referred to as a "starvation effect". There is no significant transportation of the pollutant from outside of the sampler to the sorbent material because the pollutant is not efficiently renewed. Therefore, the amount of pollutant collected by the sampler is only a very small fraction of the total amount of the pollutant in the atmosphere. To overcome the starvation effect, there should be sufficient air movement across the face of the sampler to reduce the boundary layer to zero. A minimum face velocity of 0.25 m/s is needed parallel to the open face of the sampler to maintain the concentration gradient as the driving force for diffusion (Tang et al., 1997; Hori and Tanaka, 1996; ARC, 1995; Brown, 1993; Samimi, 1987; Pozzoli and Cottica, 1987; Rose and Perkins 1982; Coulson, 1981). High face velocities can cause turbulence in the diffusional zone of the monitor. This will cause a change in the sampling rate and affect the concentration gradient. But the effect of high turbulence can be mitigated by the use of draft shields or the selection of appropriate sampling area to diffusion path length ratios (ARC, 1995; Cassinelli et al., 1987).

Another source of error is the diffusion coefficient. It is known that a gas diffusion coefficient is directly proportional to the absolute temperature raised to the three-halves power and inversely proportional to the atmospheric pressure (Lautenberger et al., 1981). The mass collected on the passive sampler is a function of

the diffusion coefficient and concentration. The concentration is directly proportional to pressure and inversely proportional to temperature from the Ideal Gas Law. Thus, the mass collected on a passive sampler is a function of the square root of temperature and not pressure. This dependency on temperature is quite small if a change in temperature of 5°C is not corrected by calculating an appropriate diffusion coefficient, the result is only less than one percent error. On the other hand, this dependency can be significant if a change in temperature from 5 to 35°C is uncorrected, will introduce a five percent error (Makkonen and Juntto, 1997; Rose and Perkins, 1982; Lautenberger et al., 1981).

Analytical procedures used in the laboratory are another form of sampling error. In order to ensure that there are no sources of sulfate (SO_4^{2-}) contamination, the filters were cleaned prior to treatment of the filters with sodium or potassium carbonate and the analytical equipment was also cleaned prior to determination of the mass of SO_4^{2-} (Alberta Health, 1997; Gagner, 1996a).

Sensitivities of time-weighted average to fluctuations in the ambient conditions when the sampling time is short result is another form of sampling bias. This was prevented by sealing the passive sampler in a container with parafilm at the end of the sampling period (Bartley et al., 1983).

Lastly, over-sampling constitutes another form of sampling bias. In the initial phase of sampling, the pollutant will occupy the active sites on the sorbent. As sampling progresses, the number of active sites on the sorbent decreases and the passive sampler approaches its capacity. The loading rate of SO_2 will decrease and this decrease will ultimately become significant enough to cause a decrease in the

concentration of the pollutant with time. Thus, the capacity or loading of the passive sampler has to be determined. A maximum recommended sampling time (MRST) has to be specified to compensate for a reduction of the sorbent's capacity (Cassinelli et al., 1987). However, over-sampling is insignificant because the volume of the diffusion path is very small and the average concentration of the diffusion path at steady state is one-half of the concentration that exists in the ambient environment (Martin, 1981).

3.4.5 Sampling Procedure for SO_2 Passive Sampler

SO_2 samplers were placed both indoors and outdoors at each of the 30 randomly selected indoor and outdoor locations in Fort McKay. The duration of the sampling period was 96 hours or 4 days. Sampling was done during the afternoon and the evening. In the fall sampling period, two to three homes were sampled daily. The maximum number of homes sampled per day was six. The sampling procedure for SO_2 samplers is summarized in Figure 3.7 (Alberta Health, 1997).

Upon arrival at a participant's home, the field staff administered the questionnaire. The home was then surveyed for a suitable location to place the sampler stands. Once the location was selected, the passive monitor was deployed according to the sampling procedure listed in Figure 3.7. The serial number of the passive monitor, along with the location of the sampler and temperature of the homes was recorded in the field logbook. Once the indoor location was secured, an additional sampler was also placed outdoors. Deployment of the samplers outdoors

were done in the same manner as listed in Figure 3.7. After approximately 96 hours, both the indoors and outdoors samplers were collected.

SO_2 Sampling Procedures

NOTE: DO NOT TOUCH THE PERMEABLE MEMBRANE (WHITE FACE) OF THE SAMPLER AT ANY TIME!

1. The samplers are packaged in a plastic transportation vial. The original shipping carton can be used to send the exposed samplers back to the laboratory for analysis.

2. Unscrew the plastic lid of the vial and remove the sampler from the can.

3. Set aside the sampler with the red button facing the ground and the permeable membrane (white face) facing up. Screw the lid back on the vial to minimize contamination.

4. Labels should be on hand. One label is attached to the **SO2 field data log sheet**.

5. Before monitoring, record the following: Sampler ID, sampling date, initiation time and relevant comments on the **SO2 field data log sheet** and **the SO2 Chain of Custody form**. Please note if the sampler was dropped or damaged and if the sampler had to placed in a less desirable location or any other comments that may be relevant.

6. Ensure that the permeation membrane (white face) is firmly attached by gently pressing down on the outside ring. **Be careful not to actually touch the white film**.

7. Attach the sampler to the stand, ensuring that the permeable membrane (white face) is facing outwards.

8. After the sampling period has ended, remove the samplers from their sampling locations. Carefully place the sampler's face down in its container.

Figure 3.7 Sampling procedure based on recommendations by Alberta Health (Gagner, 1996a).

Approximately 10% of the passive samplers were used for quality assessment and quality control (QA/QC). Blank SO_2 passive samplers were deployed, both indoors and outdoors weekly. Replicates were performed bi-weekly both indoors and outdoors. Sampling procedure for blank SO_2 passive sampler was the same as below. The blanks were treated the same as field samples. The blank sampler was also placed on the sampling stands and retrieved when the exposed SO_2 sampler was retrieved (Alberta Health, 1997; Gagner, 1996a).

3.4.6 Sampling Location of SO_2 Passive Sampler

Selecting an appropriate sampling location was very important to minimize the inconvenience placed in the selected households and to prevent the contamination of the samplers from other sources. Figure 3.8 illustrates the desired indoor and outdoor locations of the SO_2 samplers (Prince and Robb, 1999).

For indoor placement of the samplers, they were placed at least two meters away from exterior doors, windows and ventilation registers. Moreover, exterior walls and corners were avoided because they served as areas of minimum air movement. Other areas that were avoided were places that receive a lot of sunlight, areas that receive direct impact from indoor sources (i.e. gas stove), or areas where there were noticeable drafts (i.e. near open windows. and well-trafficked locations (Prince and Robb, 1999).

For outdoor placement of the samplers, they were located within one meter of trees and bushes or within five meters of any type of exhaust (i.e. clothes dryer vents, air conditioning) (Prince and Robb, 1999).

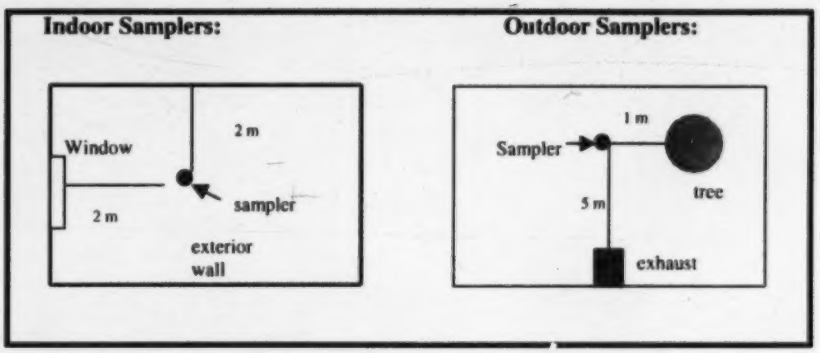


Figure 3.8 Ideal placement of the indoor and outdoor SO_2 passive samplers.

3.4.7 Laboratory Procedures

There were preliminary tests on the use of the SO_2 samplers by Alberta Health. The preliminary tests were conducted in Fort McMurray and Fort McKay. Before the SO_2 samplers were sent to the field, the filters were cleaned prior to sodium carbonate treatment and the analytical equipments were also cleaned to minimize SO_4^{2-} contamination. The mass of SO_4^{2-} on the filter was analyzed using ion chromatography (Gagner, 1996a). The labortary QA/QC procedures and analytical methods are further explained in Alberta Health and Wellness et al. (2000).

Two SO_2 samplers were exposed for 48 hours at an air monitoring station located at the entrance of Suncor Inc. in order to observe the performace of the passsive monitors. To observe the performace of the SO_2 samplers at medium and low levels of SO_2 exposures, two SO_2 passive samplers were placed at the Fort McMurray air monitoring station for 24 hours and 48 hours, respectively. Moreover, the air monitoring stations at Suncor Inc. and Fort McMurray measure SO_2 on a continuous basis with electronic equipment and it serves as a refernce method to compare the

concentration obtained by SO_2 passive monitors. Results of these tests are listed in Table 3.1 (Gagner, 1996a).

From Table 3.1, it can be seen the mass of SO_4^{2-} on the blanks were consistently lower than the the mass of SO_4^{2-} on the exposed SO_2 samplers. Moreover, there was a consistent trend of the mass of SO_4^{2-} in relation to the concentration and the time of exposure (Gagner, 1996a).

Table 3.1 Results of the preliminary evaluation of SO_2 passive sampler (taken from Gagner, 1998).

Sample Location	Sample Duration (hours)	Reference Concentration (µg/m^3)	Mass of SO_4^{2-} (µg/sampler)
Suncor	48	7.9 to 15.7 (TWA)	2.3
Suncor	48	7.9 to 15.7 (TWA)	2.9
Suncor	Blank	-	0.8
Fort McMurray	48	Non-detect to 5.3 (TWA)	1.0
Fort McMurray	48	Non-detect to 5.3 (TWA)	1.2
Fort McMurray	Blank	-	0.5
Fort McMurray	24	5.3 (TWA)	0.9
Fort McMurray	24	5.3 (TWA)	0.9
Fort McMurray	Blank	-	0.5

3.4.7.1 Interpretations of Results

The mass measured on the passive sampler is reported as "the mass of SO_4^{2-} per sampler". This mass must be converted to a TWA with a predetermined sampling rate. The sample calculation for the conversion of the mass of SO_4^{2-} per sampler to TWA of SO_2 per sampler is shown below. It is assumed that the time of exposure is 24 hours, the mass of SO_4^{2-} on the sampler is 1.5 µg and the mass of SO_4^{2-} on the blank

sampler is 0.5 μg. The mass of SO_4^{2-} per sampler is converted to mass of SO_2 per sampler using Equation 3.4 (Gagner, 1996a):

$$\text{Mass of } SO_2 = \text{mass of } SO_4^{2-} * (MW\ SO_2 / MW\ SO_4^{2-}) \qquad \textbf{(Eq. 3.4)}$$

where

MW= molar weight (g/mol)

Thus, the mass of SO_2 on the filter is 1.0 μg. Assuming mass of SO_4^{2-} on blank samplers is 0.5 μg, mass of SO_4^{2-} per blank sampler is also converted to mass of SO_2 per sampler using Equation 3.4. Thus, the mass of SO_2 on the blank filter is 0.3 μg.

Assuming desorption efficiency is 100% and storage loss and/or gain is 0%. The net amount of SO_2 on the filter is a difference between the measured value of SO_2 per sampler and the amount on the blank sampler. Thus, the amount of SO_2 per sampler is 0.7 μg.

Sampling rate is determined from exposure chamber studies to be 218 mL/min. Rearranging Equation 3.2 gives:

$$TWA = (Q/SR) * (1/t) \qquad \textbf{(Eq. 3.5)}$$

where

TWA	=	time weighted averages (μg/m^3)
Q	=	mass uptake rate (mg)
SR	=	sampling rate (ml/min)
t	=	sampling time(day)

Thus, 24 hour TWA of mass of SO_2 per sampler is 2.2 μg/m^3.

The above calculation was used for conversion of all the mass of SO_4^{2-} per sampler in the indoor and outdoor measurements taken in Fort McKay to a TWA of mass of SO_2 per sampler.

4.0 Air Exchange Collection and Analysis

4.1 Principle of Air Exchange

Air exchange is the exchange of indoor air with outdoor air as a result of infiltration or leakage and natural and mechanical ventilation (EPA, 1991; Yocom and McCarthy, 1991; Anahem Inc. et al., 1982). Infiltration and leakage are the uncontrolled movement of air through cracks and unintentional openings in the building envelope. They are induced by pressure differences between the indoor and outdoor environments. Natural ventilation is the movement of air through intentional openings such as windows or doors. It is also induced by a pressure difference between the indoors and outdoors. Mechanical ventilation is the forced movement of air between the indoors and outdoors by fans. Movement of air from the inside to the outside of a house can remove contaminants from the house. But if concentration of the contaminant is higher outdoors, then the air needs to be cleaned after it enters the building because it immediately mixes with indoor air (Anahem Inc. et al., 1982). In the case of SO_2, the outdoor concentration is generally higher than the indoor concentration. Thus, indoor levels of SO_2 can be attributed entirely to penetration from outdoors and cleaning of the outdoor air may be desirable (EPA, 1982).

Air exchange rates are expressed as the amount of air moving through the building envelope in a given length of time. It can be expressed as cubic feet per minute (ft^3/min), cubic meters per hour (m^3/hr) or volume of the building per hour (air changes per hour abbreviated as ACH) (Anahem Inc. et al., 1982).

4.2 Factors Affecting Air Exchange

There are some factors that affect air exchange such as structural parameters of a household, meteorological parameters (wind, temperature and humidity), heating, cooling and exhaust systems and the occupant's habit (Yocom and McCarthy, 1991; Coon, 1984; Meyer, 1983). In terms of the structural parameters of the house, infiltration rate is influenced by construction features of the house including quality of the construction, materials of construction and condition of the structure. Quality of the construction relates to the tightness or looseness of the house. Fewer gaps or the tighter a house is, the less infiltration or air exchange will occur. Materials of construction refers to types of windows and doors, walls and ceiling details, heating systems, wall framing details and fireplaces used in a building. Also, both the interior and exterior walls have to be considered because some materials such as brick is leakier than a framed wall. The condition of a structure refers to the age of the structure. Infiltration rate increases as the age of a house increases (Yocom and McCarthy, 1991).

A second factor that affects air exchange is meteorological parameters. Air exchange is higher for a building structure if the wind field surrounding it provides a driving force. Positive pressure is on the windward side and negative pressure is on the leeward side of the building. The orientation of flat surfaces of a building determines the magnitude of positive pressure on the windward side of the building (Yocom and McCarthy, 1991). Also, magnitude of the positive pressure is dependent on terrain and obstacles immediately surrounding a building such as vegetation or another structure (Anahem Inc. et al., 1982). The extent to which this pressure

enhances infiltration is dependent on the number, size and location of air leakage. The temperature difference between the inside and outside of the house is another meteorological parameter that affects air exchange. It is greatest in the winter when the indoor environment is heated. Temperature differences will cause differences in air density inside and outside, which will produce pressure differences. In winter, the indoor air is warmer and less dense and it rises, which is replaced by cooler and denser air entering the bottom of the structure. In summer, the reverse process occurs but the pressure difference is not as great. Thus, the magnitude of airflow associated with infiltration and exfiltration processes is more significant in the winter. Humidity can also affect air exchange. Humidity fluctuations can cause swelling and shrinking of the wood, which can alter the dimensions of the cracks. High humidity can cause swelling of the wood, which can result in low infiltration of air pollutants (Yocom and McCarthy, 1991; Godish, 1989).

The third factor that affects air exchange is the heating, cooling and exhaust systems. Type of system and duration of operation are primary factors to be considered. For combustion of fossil fuels or wood, air is extracted from the basement or living space. This air is then replaced by infiltration. The relative importance of this type of infiltration is dependent on the duration and frequency of the furnace operation (Yocom and McCarthy, 1991; Godish, 1989).

The fourth factor that affects air exchange is the occupant's habit. Activity of the occupant affects the air exchange of a building. Activities such as opening and closing of internal and external doors, operating kitchen and bathroom exhaust fans

and operating heating systems will change the impact of interior barriers to airflow (Yocom and McCarthy, 1991; Godish, 1989).

4.3 Air Exchange Measuring Technique

Air exchange rate can be measured using several approaches such as the indoor pollutant decay technique, dynamic tracer tests, passive tracer technique, fan pressurization technique and leakage area estimation (EPA, 1991; Yocom and McCarthy, 1991; Coon, 1984).

The indoor pollutant decay technique measures the decay rate of indoor pollutants as a means of calculating air exchange. Using a device, the indoor air is spiked with the non-reactive pollutant such as carbon monoxide, to an appreciable level. The device is turned off and the concentration of the pollutant is tracked over time to produce an exponential decay curve. This technique can be used only for measuring air exchange of non-reactive pollutants. In addition, the source of pollutant can be removed from indoor space or turned off after the measurement of air exchange (EPA, 1991; Yocom and McCarthy, 1991; Coon, 1984).

Dynamic tracer test is the introduction of a unique gaseous compound or tracer into the indoor space or ventilation system. Decay of the tracer is measured after adequate mixing of the tracer gas with indoor air. The tracer gas that is most commonly used is sulfur hexafluoride (SF_6). This compound is unreactive, non-toxic and can be measured at extremely low concentrations using a gas chromatograph and electron-capture detector (EPA, 1991; Yocom and McCarthy, 1991; Coon, 1984). This technique is used to obtain instantaneous or short-term air exchange rates. It

should be noted that dynamic tracer technique assumes perfect mixing of the tracer gas with the indoor air. But SF_6 is denser than air, so it has a tendency to sink and accumulate in the basement area. Moreover, inadequate air circulation may compound this effect (Coon, 1984).

Passive tracer technique is the determination of air exchange rates using permeation tubes. This method is utilized in this study. The permeation tubes emit known rates of perfluorinated methylcyclohexane (PMCH). The passive monitors (capillary absorption tube complex - CAT) are placed in the building to measure integrated concentrations of the tracer gases. The tracer emits PMCH at a known rate over a period of time and the CAT absorbs the gas at a rate that is proportional to its concentration. This technique allows the measurement of overall air exchange and the air exchange in different rooms. Also, the samples have to be exposed for long periods of time such as several hours to a week due to the miniscule quantities of PMCH emitted. Thus, the passive tracer technique is not sensitive to sudden or short-term changes in air exchange rate. Moreover, the results may be representative of a typical air exchange rate. The samples are analyzed using gas chromatography (EPA, 1991; Yocom and McCarthy, 1991; Coon, 1984; Dietz and Cote, 1982).

Fan pressurization technique involves using a calibrated fan that is mounted in one of the doors to pressurize the structure after all the normal openings are sealed. The airflow is then determined for a predetermined level of pressurization. This technique does not give air exchange rate but it gives an indication of the leakage area of the house (Yocom and McCarthy, 1991; Coon, 1984).

Lastly, leakage area estimation is another method to measure the air exchange. The calculation of air exchange rate is based on the estimation of leakage areas for wall penetrations (e.g. doors and windows) and typical leakage data for construction components (e.g. walls and ceilings) (Yocom and McCarthy, 1991; Coon, 1984). Typical leakage data are available from the American Society of Heating Refrigerating and Air Conditioning Engineers (ASHRAE Fundamentals, 1985).

5.0 Results and Discussion

Sampling procedures outlined previously were followed for all 30 randomly selected homes in Fort McKay over the course of this study. All passive monitors were exposured for a duration of approximately 4 days. All exposed passive monitors were stored in ambient conditions away from organics to minimze contamination. The passive monitors were shipped weekly to Center of Toxicology laboratory in Calgary for analysis.

5.1 Quality Assessment/Quality Control (QA/QC)

Several approaches were taken to address the quality assessment and quality control issue. Level of detection of the passive sampler was determined using blanks. Replicates and blind field blanks were also collected.

5.1.1 Calculation of Level of Detection (LOD)

The LOD was calculated from standard deviation of the blanks before the indoor and outdoor SO_2 concentrations were assessed. The results of the blank SO_2 measurements are listed in Appendix C, Table C-1. As mentioned in Section 1.3.2, Table 1.1, the LOD was chosen as 2.33σ to minimize the risk of Type I and Type II error to 1%.

$$LOD = 2.33^{*} \text{ Standard deviation for 95\% confidence} \qquad \textbf{(Eq. 5.1)}$$

where

LOD	=	level of detection
Standard deviation	=	standard deviation of the blanks

The standard deviation of the blanks was 0.34 μg of sulfate per blank filter. This was substituted into Equation 5.1 to calculate the LOD. It was 0.79 μg of sulfate per blank filter.

The mass of SO_4^{2-} was converted to the mass of SO_2 found on the passive monitors, following Equation 3.4. Thus, the equivalent mass of SO_2 on the monitors was 0.53 μg of SO_2.

From exposure chamber study, the Center of Toxicology laboratory determined the sampling rate to be 218 mL/min. The TWA of the concentration of SO_2 on the sampler was calculated using Equation 3.5. Thus, TWA of the concentration of SO_2 on the blank sampler was 0.4 $\mu g/m^3$.

The laboratory gave 2 ppb as a 24 hour LOD of SO_2. This had to be converted to $\mu g/m^3$ of SO_2, for a 96-hour TWA, assuming a standard pressure of 101325 Pa and standard temperature of 22 °C. The density of SO_2 was calculated using Equation 5.2:

$$\text{Density} = P * (MW)/RT \qquad \textbf{(Eq. 5.2)}$$

where

Density	=	density of SO_2 (g/m^3)
P	=	pressure (Pa)
MW	=	molecular weight (g/mol)
R	=	8.314 Pa m^3/mol K
T	=	temperature (K)

The density of SO_2 was 2664.8 g/m^3. This was used to convert the concentration of SO_2 in ppb to a 96-hr TWA of the concentration of SO_2. Thus, the mass of SO_2 was 1.3 $\mu g/m^3$ for a 96-hr TWA.

Since the laboratory's LOD (1.3 $\mu g/m^3$) was higher than the LOD calculated from the standard deviation of the blanks (0.4 $\mu g/m^3$), it was taken as the LOD for the SO_2 samplers. Thus, the LOD for the SO_2 samplers was 1.3 $\mu g/m^3$.

5.1.2 Accuracy and Precision of SO_2 Passive Sampler

To determine the accuracy of the SO_2 sampler, some of the samplers were co-located with samplers at the Environmental Monitoring Station in Fort McKay. The results are listed in Appendix C, Table C-2. Table 5.1 summarizes the five sets of co-located outdoor SO_2 samplers. It was found that 60% of these data were below LOD, thus a mean could not be precisely estimated.

Table 5.1 Summary of five sets of co-located outdoor SO_2 samplers.

Sample size:	5
Min:	1.3 $\mu g/m^3$
Max:	2.7 $\mu g/m^3$
Median:	1.3 $\mu g/m^3$
Mean:	Cannot estimate
% detectable:	40 %

The accuracy of the SO_2 sampler was determined by comparing measurements obtained from the co-located outdoor SO_2 samplers with measurements obtained from the Environmental Monitoring Station. Only two sets of triplicate measurements were valid from five sets of co-located samples. The other three sets of measurements were below the LOD. Table 5.2 lists the measurements obtained from the co-located outdoor SO_2 samplers and the Environmental Monitoring Station.

Table 5.2 Outdoor SO_2 measurements and the measurements obtained from the Environmental Monitoring Station in Fort McKay.

Sample #	Co-located SO_2 Samplers ($\mu g/m^3$)	Mean of the Co-located Samplers ($\mu g/m^3$)	Measurement from the Environmental Monitoring Station ($\mu g/m^3$)
1	2.6, 2.7, 2.8	2.7	2.5
2	2.1, 2.2, 2.0	2.1	1.6

$$\text{Accuracy} = \frac{(\text{mean} - \text{known})}{\text{mean}} * 100\% \qquad \textbf{(Eq. 5.3)}$$

where

mean = average measurement of the replicates

known = known concentration, in this case the measurement obtained from the Environmental Monitoring Station

For sample 1: Accuracy = (2.7 $\mu g/m^3$ -2.5 $\mu g/m^3$)/2.5 $\mu g/m^3$ * 100% = 6.4%

For sample 2: Accuracy = (2.1 $\mu g/m^3$ -1.6 $\mu g/m^3$)/ 1.6 $\mu g/m^3$ * 100% = 30%

The accuracy of the passive samplers was calculated using Equation 5.3. The accuracy was 6.4% and 30%, with an average of 18%. An acceptable level of accuracy is +/-25% as stated in the NIOSH manual (Alberta Health, 1997; NIOSH, 1977). Thus, the accuracy of the SO_2 sampler was considered acceptable.

The precision of the SO_2 samplers was determined from the relative standard deviation of the outdoor replicates. Eight sets of outdoor replicates were performed over a five-week sampling period in fall 1999. Only five sets of outdoor replicates were used to determine the precision of the SO_2 samplers, since measurements obtained from three sets of replicates were below the LOD. Precision of the SO_2

passive sampler was calculated from the relative standard deviation (RSD) of the replicates using Equation 5.4. Table 5.3 summarizes the results.

$$RSD = \frac{\text{standard deviation}}{\text{mean}} * 100\% \qquad \textbf{(Eq. 5.4)}$$

where

standard deviation	=	standard deviation of the replicates
mean	=	mean of the sample set

Table 5.3 Replicated outdoor SO_2 measurements, mean and RSD for Fort McKay study.

Sample #	Replicates ($\mu g/m^3$)	Mean ($\mu g/m^3$)	Standard Deviation ($\mu g/m^3$)	RSD*
12	1.5, 1.8	1.6	0.2	13%
14	1.6, 1.6	1.6	0	1.4%
19	1.3, 2.2	1.8	0.6	34%
20	2.5, 2.2	2.3	0.2	7.0%
21	2.6, 2.3	2.5	0.2	7.2%

***RSD= Relative Standard Deviation**

The RSD ranges from 1.4% to 34%, with a mean of 13% and a median of 7.2%. A workable precision between replicates is +/-25% as stated by NIOSH manual (Alberta Health, 1997; NIOSH, 1977). Thus, the precision of the SO_2 sampler was considered acceptable. Moreover, the standard deviation of each set of replicates ranges from 0 to 0.6 $\mu g/m^3$. The standard deviation was very small, thus there was not much variation between replicates.

5.1.3 Quality Assurance of Laboratory Analysis

Center of Toxicology laboratory in Calgary analyzed the SO_2 passive samplers in the Fort McKay study. To determine the quality of laboratory analysis, blind field blanks, which are unopened new samplers, were sent to the laboratory and labeled as exposed field samplers. Nine blind field blanks were sent in week two and week five of the sampling period. The results of the blind blank SO_2 passive samplers are listed in Appendix C, TableC-3. No traces of SO_2 should be detected on the blind blank samplers. The average SO_2 concentrations on the blind blank samplers was 1.0 $\mu g/m^3$, which is below the LOD (1.3 $\mu g/m^3$). Therefore, the quality of the laboratory analysis was considered good.

5.2 Summary of Indoor SO_2 Measurements

Indoor SO_2 measurements were taken in 20 houses and 10 trailers. Table 5.4 summarizes the indoor SO_2 measurement for the fall 1999 sampling period. Individual indoor SO_2 results are listed in Appendix C, Table C-4. It should be noted that when replicates were performed, the SO_2 measurement was a result of the average of these replicates.

Tables 5.4 Summary of indoor SO_2 measurements of 30 homes taken in late fall 1999.

Sample Size:	30
% detectable:	0%

All of the indoor SO_2 concentrations were less than the LOD (1.3 $\mu g/m^3$). Thus, it can be concluded that the indoor SO_2 levels were minimal. No statistical

analysis was done on the indoor SO_2 measurements because of the high levels of non-detectable measurements.

The indoor SO_2 measurements are comparable to indoor measurements taken from six American cities and from the rural community of Boyle, Alberta where indoor levels ranged from 1 to 22 $\mu g/m^3$ and 0.2 to 2.3 $\mu g/m^3$, respectively (Kindzierski and Sembaluk, 1998; Spengler et al., 1979). Indoor concentrations of SO_2 are also comparable to winter measurements obtained in Boston, MA where average indoor SO_2 measurements were 1.0 $\mu g/m^3$ (Brauer et al., 1991). However, indoor concentration of SO_2 in Fort McKay is lower than the reported indoor concentration of SO_2 in the urban community of Sherwood Park, Alberta and in Korea, which ranged from 0.9 to 5.2 $\mu g/m^3$ and 6.2 $\mu g/m^3$, respectively (Kindzierski and Sembaluk, 1998; Lee et al., 1997). The low concentrations of SO_2 in Fort McKay may be a result of decreased industrial emission and vehicular traffic in rural areas as opposed to the urban centers of Sherwood Park, Alberta and Korea.

5.3 Summary of Outdoor SO_2 Measurements

Outdoor SO_2 measurements were retrieved for 19 houses and 10 trailers in late fall 1999. One SO_2 passive sampler from a participating house was lost in the field. Table 5.5 summarizes the outdoor SO_2 measurements. Individual outdoor SO_2 measurements are listed in Appendix C, Table C-5.

Table 5.5 Summary of unadjusted outdoor SO_2 measurements of 29 homes taken in late fall 1999.

Sample size:	29
% detectable:	66%
Min:	1.3 $\mu g/m^3$
Max:	9.5 $\mu g/m^3$
Median:	1.6 $\mu g/m^3$
Mean:	1.9 $\mu g/m^3$
95% Confidence Interval for the mean:	1.3 <x> 2.6
Standard Deviation:	1.7 $\mu g/m^3$
Variance:	2.9 $\mu g/m^3$
Standard Error:	0.3

The outdoor SO_2 concentration ranged from 1.3 $\mu g/m^3$ to 9.5 $\mu g/m^3$, with an average of 1.9 $\mu g/m^3$ and a median of 1.6 $\mu g/m^3$. Sixty-six percent of the outdoors SO_2 measurements were above the LOD. Since more than 15% of the outdoor measurements were below the LOD, an alternative method had to be employed to calculate the mean of the outdoor measurements instead of simply averaging all of the outdoor data.

Before the mean was calculated, there were some concerns about two outdoor measurements that were collected. From Appendix C, Table C-5, one replicate measurement (29 $\mu g/m^3$) was thrown out since it was not in the vicinity of the other measurements and it was considered much higher than the whole outdoor data set. From Table C-5, another data point (9.5 $\mu g/m^3$) was tested to determine whether it was an outlier. The Q-Test was administered to determine this (Harns and Kratochvil, 1981):

$$Q = \frac{\text{suspect value - nearest value}}{\text{largest value - smallest value}} \qquad \textbf{(Eq. 5.5)}$$

where

suspect value = suspected outlier
nearest value = the nearest value to the outlier
largest value = largest value in the data set
smallest value = smallest value in the data set

According to Equation 5.5, the Q-Test calculated value was 0.63. This was compared to the tabulated Q-Test values at 90% confidence level listed in Table 5.6 below.

Table 5.6 Tabulated Q-Test values at 90% confidence level (taken from Harris and Kratochvil, 1981).

Sample Size	Q at 90%
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

If the Q-Test calculated value exceeds the Q-Test tabulated value, then the suspected outlier is removed from the data set. From Table 5.6, it can be seen that as the sample size increases, Q-Test tabulated values decrease. Thus, the Q-Test tabulated value for a sample size of 29 would be smaller than 0.41. The Q-Test calculated value was 0.63. Therefore, the calculated Q-Test value was larger than the

Q-Test tabulated value, and 9.5 $\mu g/m^3$ was considered an outlier and was removed from the outdoor data set.

The mean of the outdoor measurements can be calculated using several methods such as the Median method, Trimmed Mean method and Windorized Mean method, for censored data sets. The Median requires that less than 50% of the data are below LOD, Trimmed Mean requires that less than 25% of the data are below LOD and Windorized Mean requires that less than 15% of the data are below LOD. Since 34% of the outdoor measurements were below the LOD, the Median method was used. In this approach, it is stated that the mean and the median are the same value, which is 1.6 $\mu g/m^3$ (Berthouex and Brown, 1994).

There are many ways to treat below LOD data (Berthouex and Brown, 1994):

- Replace the censored values with LOD value
- Replace the censored values with zeros
- Replace the censored values with half LOD value
- Eliminate the values that are below LOD

For this data set, the outdoor SO_2 measurements that were below LOD were replaced with half the LOD (0.7 $\mu g/m^3$). This method is also used by Wallace et al. (1987) for analysis of indoor/outdoor air quality data sets.

The analysis of outdoor SO_2 measurements were re-calculated using the Median method and replacement of the below detection data with ½ LOD. An adjusted summary of the outdoor SO_2 measurements is listed in Table 5.7.

Table 5.7. Adjusted summary of outdoor SO_2 measurements taken from 28 households in late fall 1999.

Sample size:	28
% detectable:	64%
Min:	1.3 µg/m³
Max:	3.6 µg/m³
Median:	1.6 µg/m³
Mean:	1.6 µg/m³
95% Confidence Interval for the mean:	1.3 <x> 2.0
Standard Deviation:	0.9 µg/m³
Variance:	0.7 µg/m³
Standard Error:	0.1

Outdoor SO_2 levels ranged from 1.3 µg/m³ to 3.6 ug/m³, with an average of 1.6 µg/m³. The cumulative frequency of the outdoor SO_2 measurements is shown in Figure 5.1. Thirty-six percent of the measurements were below LOD. Twenty- nine percent, 14%, 11% and 10% of the outdoor measurements occurred between 1.5 - 2.0 µg/m³, 2.0 – 2.5 µg/m³, 2.5 – 3.0 µg/m³ and 1.3 - 1.5 µg/m³ respectively. Only 3.6% of the outdoor SO_2 measurements were above 3.0 µg/m³.

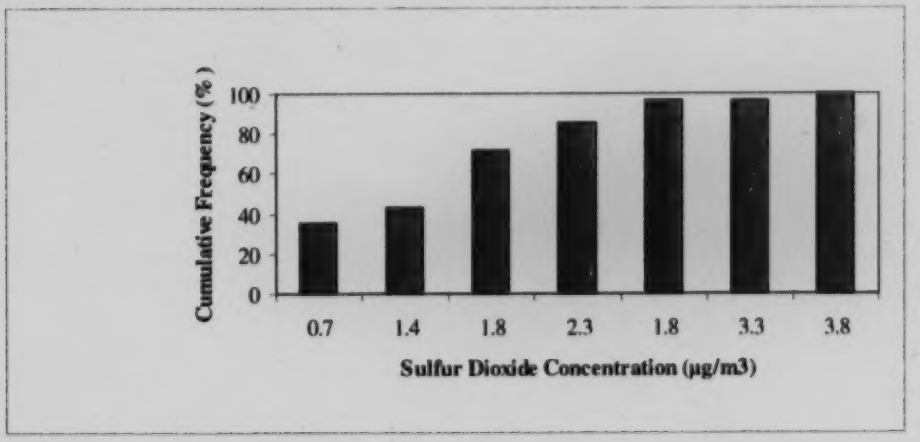


Figure 5.1 Cumulative frequency of 28 outdoor SO_2 measurements taken in late fall 1999.

The outdoor SO_2 measurements in Fort McKay are comparable to the outdoor SO_2 measurements of five rural communities in Saskatchewan taken from October 1985 to March 1986. These results are lower than reported outdoor SO_2 measurements in the rural community of Boyle, Alberta, which ranged from 3.7 to 5.6 $\mu g/m^3$ (Kindzierski and Sembaluk, 1998). In addition, the outdoor concentration of SO_2 in Fort McKay was lower than reported concentrations of SO_2 in urban centers such as Sherwood Park (9.9 $\mu g/m^3$), Edmonton (8 $\mu g/m^3$), Vancouver (11 $\mu g/m^3$), Toronto (14 $\mu g/m^3$) and Montreal (16 $\mu g/m^3$) (Hrudey and Kindzierski, 1998).

5.4 Comparison of Indoor/Outdoor SO_2 Measurements

Indoor and outdoor SO_2 concentrations are plotted in Figure 5.2. The indoor concentrations of SO_2 were lower than the outdoor concentrations. This finding is consistent with previous studies. SO_2 is primarily an outdoor pollutant, which results from the combustion of fossil fuels in industrial processes and for transportation. Moreover, the levels of SO_2 indoor and outdoor were lower than the Alberta and Canadian air quality guidelines established for the protection of human health, which is 150 $\mu g/m^3$ over 24 hour (short term exposure) or 30 $\mu g/m^3$ over 1 year (long term exposure). Thus, it can be concluded that oil sands activities did not increase SO_2 levels in the indoor and outdoor microenvironments to levels intended for human health protection during the period of monitoring (fall 1999).

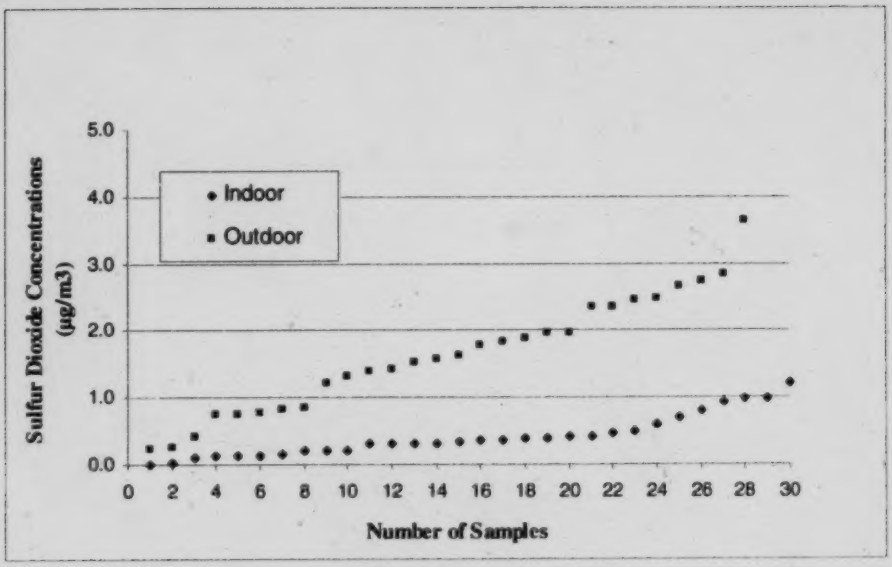


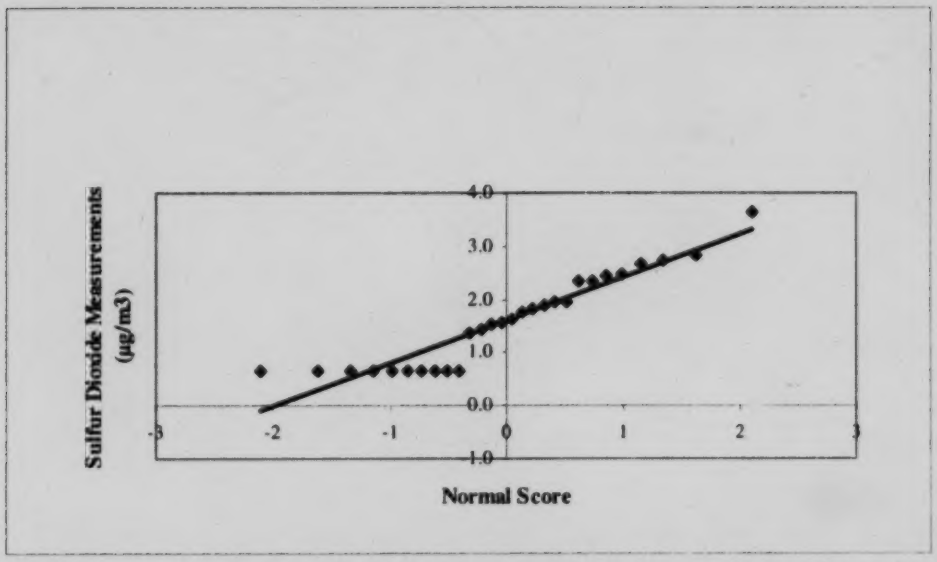
Figure 5.2 Indoor and outdoor SO_2 concentrations based on 96 hour TWA for 30 residences in Fort McKay in late fall 1999.

5.5 Comparison of Outdoor and Environmental Monitoring Station SO_2

Measurements

In order to determine whether to use parametric or non-parametric tests for statistical analysis of the outdoor SO_2 measurements, the data were plotted in a normal probability plot to see if it was normally distributed. If the normality plot is a straight line, parametric statistics can be used in statistical analysis of the outdoor SO_2 data. If the normality plot is not a straight line, then non-parametric statistics should be used. Figure 5.3 shows the normal probability plot of the outdoor SO_2 measurements.

From Figure 5.3, it can be seen that a straight line can be fitted to the normal probability plot of the outdoor SO_2 measurements. Thus, the outdoor data are normally distributed and parametric tests were used for the statistical analysis.



Note: The horizontal values in the beginning are representative of non-detectable data.

Figure 5.3 Normal probability plot of 28 outdoor SO_2 measurements.

In Fort McKay, there is continuous monitoring of outdoor levels of SO_2 by the Wood Buffalo Environmental Association. The Environmental Monitoring Station, shown in Figure 5.4, measures 1-hour averages of outdoor SO_2 concentrations and it is located 5 minutes away from Fort McKay. The averaged daily concentrations of SO_2 from the Environmental Monitoring Station, along with meteorological data are listed in Appendix D for the same time period in which indoor/outdoor passive sampling was conducted. Before conducting this study, there was some debate as to the validity of this approach as a true representation of SO_2 in the community. The concerns were based on the distance of the station from the affected community.

Figure 5.4 Environmental Monitoring Station in Fort McKay.

In order to determine if there were any differences between outdoor SO_2 measurements and SO_2 measurements obtained from the Environmental Monitoring Station, Paired sample t-test was employed (Zar, 1996). The basic assumption of the Paired sample t-test is that the difference between outdoor SO_2 measurements and SO_2 measurements obtained from the Environmental Monitoring Station must be normally distributed (Zar, 1996; Mendenhall and Sincich, 1995; Bowker and Lieberman, 1972). The outdoor SO_2 measurements and SO_2 measurements obtained from the Environmental Monitoring Station are listed in Appendix E. Figure 5.5 shows a normal probability plot of the difference between the outdoor SO_2 measurement and the SO_2 measurement obtained from the Environment Monitoring Station. It can be seen that a straight line can be fitted to normal probability plot of the difference between the outdoor SO_2 measurement and the SO_2 measurement obtained from the Environment Monitoring Station. Therefore, the difference is normally distributed and the basic assumption of the Paired sample t-test was satisfied.

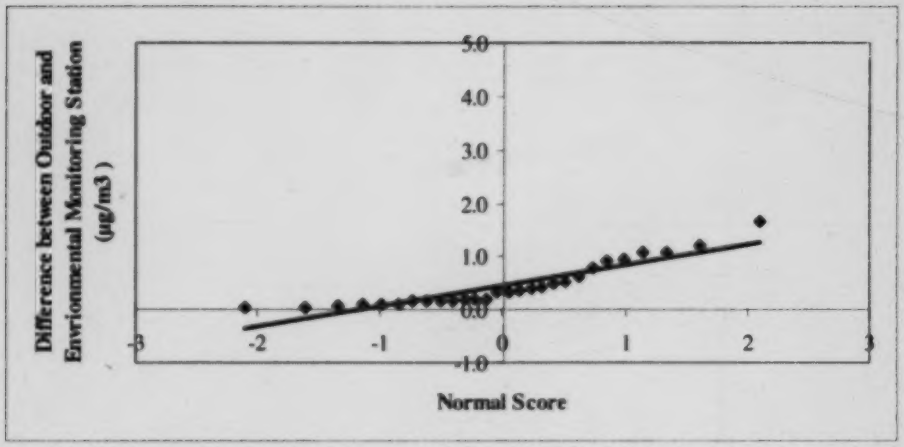


Figure 5.5 Normal probability plot of the difference between the 28 outdoor SO_2 measurements and SO_2 measurements obtained from the Environmental Station in Fort McKay.

The null hypothesis (H_o) of the Paired sample t-test states that the mean difference between the outdoor SO_2 measurements and the SO_2 measurements obtained from the Environmental Monitoring Station is zero. The alternative hypothesis (H_A) of the Paired sample t-test states that the mean difference between the outdoor SO_2 measurements and the SO_2 measurements obtained from the Environmental Monitoring Station is not zero (Zar, 1996; Mendenhall and Sincich, 1995; Bowker and Lieberman, 1972):

Null hypothesis: H_o: $u_d = 0$

Alternative hypothesis: H_A: $u_d \neq 0$

where u_d = difference between the outdoor SO_2 measurements and the measurement obtained from the Environmental Monitoring Station

$t_{cal} = d/s_d = 0.14/0.11574 = 1.21$

$t_{0.05\,(2)\,27} = 2.052$

$t_{cal} < t_{crit}$, therefore failure to reject H_o.

From the calculations presented above, it was concluded that there was no difference between measurements obtained from 28 randomly chosen locations in Fort McKay and measurements obtained from the Environmental Monitoring Station in Fort McKay. Thus, the measurements obtained from the Environmental Monitoring Station was a good representation of outdoor levels of SO_2 in the community.

5.6 Air Exchange Measurements

The air exchange measurements were conducted using the passive tracer technique. It was retrieved for 17 houses and 7 trailers in the community of Fort McKay. Air exchange devices were lost for 3 houses and 3 trailers. The results are listed in Appendix F. Placement of the PMCH sources and CATs were in spaces of relatively free movement of air. Areas such as windows, doors or areas of strong drafts or winds were avoided. Moreover, they were placed no closer than 1.9 meters from each other. CATs were suspended or placed on a flat surface with the exposed end protruding beyond the end of the surface. Three PMCH sources were deployed in each of the households in the initial visit. Two CATs were deployed after 24 hours in each of the households. Ninety-six hours after the initial visit, the PMCH sources and the CATs were retrieved separately and placed in different locations to minimize the contamination of the deployed CATs by the PMCH sources. In addition, 10% of the deployed CATs served as duplicate samples and 10% of the deployed CATs served as

field blanks. Robert Weker from School of Public Health (Boston, MA) determined the air change rate (ACH) for each of the households using the protocol listed in Appendix G (Weker, 1999).

The average ACH for 24 households was 0.38 ACH with a standard deviation of 0.17 ACH and a median of 0.37 ACH. The percent cumulative frequency for the ACH for 24 households is shown in Figure 5.6. It can be seen that 15% of the air exchange data from 24 households were in the range of 0.21 – 0.25 ACH and 0.46 – 0.50 ACH, respectively.

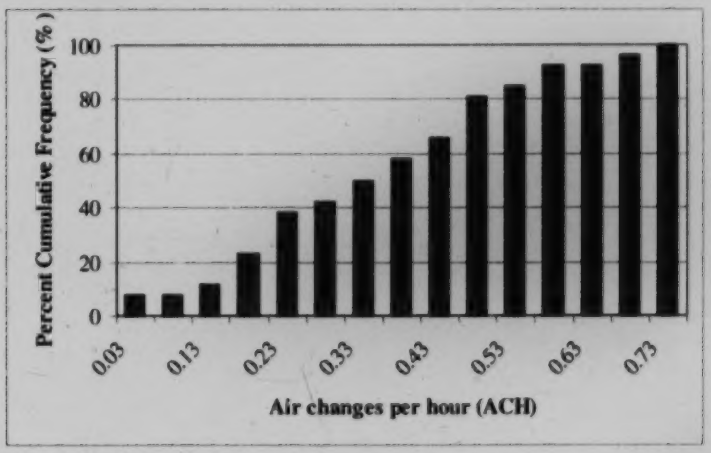


Figure 5.6 Cumulative frequency of air exchange in 24 homes in Fort McKay.

From the 24 sampled households, 4% of the homes were built in the 1960s, 11% of the homes were built in the 1970s, 36% of the homes were built in the 1980s and 32% of the homes were built in the 1990s. For 17% of homes, the construction dates were not known. Thus, the majority of the sampled households were built in the 1980s and 1990s. The air exchange rates in Fort McKay are comparable to studies

conducted by Grimsrud *et al.* (1983), where it was found that homes built during or after 1970 have an average ACH of 0.46. The ACH of homes in Fort McKay is also comparable to studies conducted in Canada and northern regions of United States where the ACH ranged from 0.1 – 2.5 ACH and 0.01 – 2.4 ACH, respectively (Otson et al., 1998; Murray and Burmaster, 1995).

From the air exchange measurements of houses and trailers in Fort McKay, it can be concluded that the households have minimum indoor/outdoor air flow. Therefore, the majority of the indoor sources of SO_2 may not result from infiltration from outdoors but it is a result of local indoor sources.

For the duplicate samples, relative standard deviation (RSD) of air exchange measurements was calculated to express sample variability relative to the mean of the sample. This was used to determine the precision of the passive tracer technique. The relative standard deviation for the duplicate samples ranged from 0% to 8.4%, with an average of 4.2%. Thus, the relative standard deviation was small, and the passive tracer technique was precise.

6.0 Conclusions and Recommendations

The purpose of this study was to measure baseline indoor and outdoor levels of sulfur dioxide (SO_2) along with air exchange measurements in Fort McKay, Alberta in order to determine whether proximity to oil sands activities affects air quality in the community.

This study was conducted in fall 1999. Thirty households were chosen using a random stratified sampling procedure. This resulted in a sample size of 20 houses and 10 trailers. SO_2 and air exchange measurements were taken using a passive sampler and passive tracer technique respectively. Paired sample t-test was used for statistical analysis of the data obtained.

The validity (accuracy and precision) of the SO_2 passive samplers was evaluated by making comparisons to a continuous environmental monitoring station in Fort McKay. Accuracy was assessed with two sets of triplicate measurements. The accuracy of the passive sampler was 18%. Precision of SO_2 passive sampler was assessed from replicated outdoor SO_2 measurements. Five sets of replicated outdoor measurements were used and precision was found to be 13%. Thus, accuracy and precision of the passive samplers were within National Institute of Occupational Safety and Health workable guidelines of +/- 25%.

The Center of Toxicology laboratory in Calgary, Alberta was responsible for the analysis of the passive samplers. For quality assurance and to determine the accuracy of the laboratory procedures, nine blind blanks labeled as field blank SO_2 samplers were assessed. The average concentration obtained from the blank SO_2 samplers was 1.0 $\mu g/m^3$, which was below the LOD (1.3 $\mu g/m^3$).

The level of detection (LOD) for the SO_2 passive sampler was 1.3 $\mu g/m^3$. None of indoor concentrations of SO_2 were above the LOD. Out of 30 outdoor measurements that were taken, one sampler was lost and one measurement was considered invalid. Outdoor SO_2 measurements of 28 households ranged from 1.3 $\mu g/m^3$ to 3.6 $\mu g/m^3$ (mean: 1.6 $\mu g/m^3$; standard deviation: 0.9 $\mu g/m^3$). Eighteen out of 28 outdoor SO_2 measurements (64%) were above the LOD. Thus, indoor levels of SO_2 were lower than the outdoor levels of SO_2 consistent with SO_2 being an outdoor air pollutant.

Despite detectable outdoor SO_2 levels, these levels remained low in comparison with Alberta and Canadian air quality guidelines intended for protection of human health – 150 $\mu g/m^3$ over 24 hour (short term exposure) or 30 $\mu g/m^3$ over 1 year (long term exposure). It was found that oil sands activities did not increase SO_2 levels in indoor and outdoor microenvironments to levels intended for human health protection during the period of monitoring (fall 1999).

Outdoor SO_2 measurements were compared with levels of SO_2 in rural communities in North America subjected to long range transport of airborne pollutants, as well as urban centers in North America and Asia. Urban centers have increased industrial and vehicular activities. These activities contribute to increased levels of air pollutants, including SO_2. Data obtained from rural communities in Saskatchewan (October 1985 to March 1986) (mean = 1.1 $\mu g/m^3$), were comparable to outdoor SO_2 measurements in Fort McKay (mean = 1.6 $\mu g/m^3$). Urban outdoor measurements taken in fall 1998 in Sherwood Park, Alberta (mean = 9.9 $\mu g/m^3$), an urban community, were higher than outdoor SO_2 measurements in Fort McKay.

A single continuous environmental monitoring station is used for measurement of SO_2 levels in Fort McKay. Before conducting this study, there was debate as to the validity of this approach as a representation of SO_2 exposure in the community. At issue was the distance of the station from the affected community. The station reports meteorological measurements as well as an hourly average of SO_2. These measurements were compared to outdoor SO_2 measurements with passive samplers, taken at 28 random locations around the study area. Paired sample t-test was used for statistical analysis and no difference was found between the two measurements ($p<0.05$). Thus, measurements obtained from the environmental monitoring station, situated five minutes from the town, are a good representation of outdoor SO_2 levels across Fort McKay.

Air exchange measurements were retrieved for 24 out of 30 households sampled. Air exchange ranged from less than 0.01 ACH to 0.73 ACH, with a mean of 0.38 ACH (standard deviation of 0.17 ACH). Average air exchange rates in Fort McKay were comparable to typical air exchange rates in Canada and northern regions of United States (range: 0.3 to 0.5 ACH). Moreover, it can be concluded that the households have minimum indoor/outdoor air flow. Therefore, the majority of the indoor sources of SO_2 may not result from infiltration from outdoors but it is a result of local indoor sources.

This study has generated new possibilities for future research. The main recommendation would be to increase the sampling period for SO_2 passive samplers. In this study, the sampling time was a period of four days, which did not result in a significant difference between indoor and detectable (LOD) concentrations of SO_2.

Thus, increasing the sampling period to seven days or greater, would result a greater number of sample measurements to be above the LOD. Another recommendation would be to test for the seasonal variation of SO_2. The indoor and outdoor levels of SO_2 should be measured in the fall and winter because the levels of SO_2 are perceived to be higher in these time periods.

7.0 References

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Appendix A. Recruitment Package

Fort McKay Air Quality and Exposure Study

Recruitment Status Form

Section A. Household Identification

List No. :		(refer to Recruitment List)
Household Unit No.:		
Housing Type:		(house or trailer)

Section B. Record of Recruitment Visits

Day of Week	Date	Time	Result (refer to list of possible results below)

Possible Results

- VACANT
- NO ONE HOME (followup visit required)
- NEEDS MORE INFO (followup visit required)
- AGREED TO TAKE PART (complete Section C)
- REFUSED TO TAKE PART (give reason if possible)

Recruit Consent Form

Sampling Unit: _____

Title of Project: ***COMMUNITY AIR QUALITY AND EXPOSURE ASSESSMENT IN FORT MCKAY, ALBERTA***

Please complete this short form:

Do you understand that you have been asked to be in a research study?	Yes	No
Have you read and received a copy of the Information Sheet?	Yes	No
Have you received and read a copy of the Information Sheet	Yes	No
Have you had a chance to ask questions and discuss this study?	Yes	No
Do you understand that you are free to refuse to take part or withdraw from the study at any time? You do not have to give a reason.	Yes	No
Do you understand that all information collected fort this study is private And that your name will not be used in any reports on this study?	Yes	No

This study was explained to me by: _____
Name of field worker

I agree to take part in this study_____
Signature of participant/ Date

_____ _____
Name of participant (please print) Phone No (optional)

I believe that the person signing this form understands what is involved in the study and voluntarily agrees to participate:

_____ _____
Signature of field worker Date

Appendix B. Questionnaire

Ft. McKay Air Quality Study
HOUSEHOLD CHARACTERISTICS (Q1)

Sample #: _____ Interviewer: _____

Date: _____

Title of Project: ***COMMUNITY SAMPLING OFPARTICULATE MATTER, SULPHUR DIOXIDE AND VOLATILE ORGANIC COMPOUNDS IN FORT McKAY***

Principal Investigator: Warren Kindzierski
University of Alberta

Co-Investigators: Madeline Delisle
Margaret MacDonald, Shirley Ford and Maureen Grandjambe

Field Investigators: Russ Miyagawa, Bettina Mueller, Sunita Ranganathan
University of Alberta
Phone: 492-8548

Instructions:

The information obtained by this questionnaire will be held in strict confidence and will be used for research purposes only. All results will be summarized for groups of people; no information regarding individual persons will be released without the consent of the individual.

Your answers help to determine things about your home that may affect indoor air quality. Before you answer a question as "unknown", please refer to the glossary of terms for unfamiliar words or ask your interviewer for help.

Thank you for your co-operation.

A. Household and Participant Identification:

1. Participant Name: _____
2. Participant Phone No.: _____
3. Street Address, P.O. Box _____
4. City/Hamlet: _____

B. Household Habitants:

5. Who lives in the house?

Person #	Name (optional)	Age Category *	Smoker (y/n)	Occupation
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

- Age Categories: **1** = 0-12 years; **2** = 12-17 years; **3** = 18 years and over

Are there any pets in your household?

☐ yes ☐ no

If yes, what kind of pets do you have?

☐ dog ☐ cat ☐ other _____

C. Type of House

6. Which best describes your home?

☐ a mobile home or trailer

☐ a one-family house detached from any other house

7. **How big is the house, without the basement?**

_____ square feet, or _____square metres ☐ check box if estimated

8. **Do you have a finished basement?**

☐ yes ☐ no ☐ unknown

9. **How big is the basement?**

_____ square feet, or _____square meters ☐ check box if estimated

10. **In what year was the house originally built?**_____

11. **Is there an unpaved driveway on your property?**

☐ yes ☐ no

12. **Is there a garden on your property**

☐ yes ☐ no

13. **Do you have an outdoor barbecue, firepit or burnbarrel?**

☐ yes ☐ no

14. **Do you have a smokehouse?**

☐ yes ☐ no

15. **While you are awake, in which area of your home do you spend MOST of your time?**

☐ bedroom ☐ kitchen

☐ spare room ☐ living room

☐ dining room ☐ rec room

☐ other_____

D. Heating, Ventilation, and Air Conditioning Systems:

16. **Does the house have an air conditioner?**

☐ yes ☐ no ☐ unknown

If yes, what type? ☐ central ☐ room

If it is a room air conditioner, what room is it in?_____

17. **Does the house have any fans for extra ventilation?**

☐ yes ☐ no ☐ unknown

If yes, what type(s)?

☐ portable fan ☐ ceiling fan ☐ bathroom fan

Location(s)?_____

18. Does the house have an air purification system installed?

☐ yes ☐ no ☐ unknown

If yes, what type?_____

19. Does the house have any range hoods, fume hoods?

☐ yes ☐ no ☐ unknown

If yes, where is it? _____

Where does it vent to?

☐ outside ☐ inside ☐ unknown

20. Have you had your gas pipes/gas appliances checked for leaks?

☐ yes ☐ no ☐ unknown

If so, when? _____

21. How do you heat your home? Where are the heaters located?

Type of System	Main	Second	Third	Location
forced air furnace	☐	☐	☐	_____
gravity furnace	☐	☐	☐	_____
radiant heat – wall	☐	☐	☐	_____
radiant heat – floor	☐	☐	☐	_____
fireplace	☐	☐	☐	_____
stove	☐	☐	☐	_____
room heater	☐	☐	☐	_____
portable heater	☐	☐	☐	_____
other _____	☐	☐	☐	_____

22. What type of fuel do you use?

Type of fuel	Main	Second	Third
natural gas	☐	☐	☐
fuel oil	☐	☐	☐
electricity	☐	☐	☐
kerosene	☐	☐	☐
wood	☐	☐	☐

other _____ ☐ ☐ ☐

23. Do you keep the house at the same temperature all the time?

☐ yes ☐ no ☐ unknown

24. Does the heating system have a combustion air supply?

☐ yes ☐ no ☐ unknown

25. Does the heating system have a fresh air return?

☐ yes ☐ no ☐ unknown

26. Do you use a humidifier

☐ room humidifier ☐ attached to furnace ☐ no

☐ unknown

27. Do you have a sump pump?

☐ yes ☐ no ☐ unknown

E. Attached Structures:

28. Does the house have any attached structures?

☐ yes ☐ no ☐ unknown

If yes, what type(s)?

☐ garage ☐ shed/shop ☐ porch

☐ greenhouse ☐ other _____

If no then go to Question 33.

29. Do you start your vehicle in the garage?

☐ yes ☐ no ☐ unknown

If yes, what type of fuel does it uses?_____

30. Does the attached structure(s) have a door that opens into the house?

☐ yes ☐ no ☐ unknown

If yes, is this door(s) usually left open or closed?

☐ yes ☐ no ☐ unknown

31. Does the attached structure have a heating system?

☐ yes ☐ no ☐ unknown

If yes, what type? _____

Please use the categories listed in question (21,22).

32. Does the attached structure have any ventilation or exhaust system(s)?

☐ yes ☐ no ☐ unknown

If yes, what type?

☐ window/overhead door ☐ exhaust system ☐ fan

If exhaust, where does it vent to? ☐ outside ☐ inside

F. Household Sources of VOCs, PM, SO_2:

33. Are all of your household appliances (cooking stove, hot water heater, clothes dryer, etc.) electric? If no, please complete the below table.

☐ yes ☐ no ☐ unknown

	Type of Fuel (✔)		
Type of Appliance	natural gas	other (specify)	location
cooking stove			
hot water heater			
clothes dryer			
other _____			

34. Do you ever use the cooking stove for heating your home?

☐ yes ☐ no ☐ unknown

35. Is the clothes dryer vented to the outside?

☐ yes ☐ no ☐ unknown

36. Do you have carpet in your home?

☐ yes ☐ no ☐ unknown

37. How much carpet would you guess your home has?

☐ <25% ☐ 25 to 50% ☐ 50 to 75% ☐ >75%

38. Has any part of the house had carpet installed within the past year?

☐ yes ☐ no ☐ unknown

If yes, than within past: ☐ 3 months ☐ 6 months

Where was it installed? _____

39. Do people smoke inside the house or any of the attached structures?

☐ yes ☐ no ☐ unknown

Comments:

_____

_____

_____

_____

_____

_____

_____

_____

End of Questionnaire

GLOSSARY OF TERMS:

If the term you are looking for is not here or you still do not understand the question then please contact one of the investigators.

attached structure a building which is physically connected to your home. This may include a garage, shed, shop, greenhouse, etc.

combustion air supply an insulated air duct which supplies fresh air from outside to the furnace room for combustion. It is not directly attached to the furnace and it usually ends just above the floor with a perforated cap.

duct a pipe or conduit which moves air.

exhaust system an electric fan which draws air out of an area and blows it outside (vents outside), or an electric fan which circulates the air through a filter and blows it back inside (vents inside).

fireplace/stove a wood, gas, or coal fueled fire burning unit.

forced air furnace this is a furnace where the warm air is pushed through the furnace ducts by the furnace's electric fan.

fresh air return an (insulated) air duct which supplies fresh air from outside to the furnace as a fresh air supply for the house. It is directly attached to the furnace's air intake duct.

gravity furnace an older style furnace where the warm air rises naturally through the furnace ducts without the aid of a fan.

mechanical a motorized system requiring power to run.

portable heater a portable heater which is usually fueled by propane, kerosene, or electricity.

radiant heat a heating system which circulates hot water from a boiler throughout the house. The heat from the hot water is given off of pipes that run along the base of a wall, or run underneath the floor.

room heater	a fixed heater located in a specific room, usually intended to supplement the main heating system.
single family house	a house which was originally designed to accommodate a single family. This does not include a duplex, a fourplex, an apartment building or any other multifamily housing.
vent	process of blowing air or fumes usually out the end of a pipe. If the air is blown to the outside than this is venting outside, if the air is blown back inside of the house than this is venting inside.
ventilation	the movement of air in a space. It can be either mechanical ventilation through the use of an electric fan, or it can be natural ventilation achieved by opening windows or doors.

FORT MCKAY AIR QUALITY STUDY

Personal Exposure and Activity Questionnaire (Q2)

Sample No: _____ Interviewer: _____

Date: ____ / ____ / ____

1. **Did you have your drapes, carpet, or furniture professionally cleaned during the past 24 hours?**
   ☐ Yes ☐ No

2. **Did you vacuum your home during the past 24 hours?**
   ☐ Yes ☐ No

3. **Were any windows or outside doors left open in your home during the past 24 hours?**
   ☐ Yes ☐ No

4. **Have you used tobacco, in any form, during the past 24 hours?**
   ☐ Yes (GO TO QUESTION 4a) ☐ No (GO TO QUESTION 5)

   a) **Which of the following tobacco products have you used in the past 24 hours?**
   ☐ Cigarettes ☐ Cigars ☐ Pipe ☐ Snuff ☐ Chewing tobacco

   b) **Approximately how many cigarettes did you smoke during the past 24 hours?** _____

5. **Were you exposed to second-hand tobacco smoke during the past 24 hours (in enclosed area with active smokers for more than 15 minutes)?**
   ☐ Yes ☐ No

   a) **For how long were you exposed to second-hand smoke during the past 24 hours?** _____

6. **Were you exposed to any other smoke (forest or camp fires, smoke houses, etc.) during the past 24 hours? If yes, please specify the source(s) of the smoke.**
   ☐ Yes (specify below) ☐ No
   Specify:
   _____

7. **Have you used or worked with insecticides, pesticides, or herbicides in the past 24 hours?**

☐ Yes ☐ No

8. **Did you use a portable fan or a humidifier in the last 24 hours?**

☐ Yes (specify below) ☐ No

Where?_____

9. **Did you use clothes dryer in the last 24 hours?**

☐ Yes ☐ No

10. **Have you operated any gas-powered appliances or tools in the past 24 hours? If specify the appliance or tool and type of fuel.**

☐ Yes (specify below) ☐ No

	Appliance/Tool	Fuel
1.	_____	_____
2.	_____	_____
3.	_____	_____

11. **Have you traveled by car, truck or other gas-powered vehicle in the past 24 hours? Have you walked or bicycled near a major roadway in the past 24 hours?**

☐ Yes (Specify.) ☐ No (GO TO QUESTION 12)

Please provide details of any trips you have made:

Trip	Type of Vehicle	Duration	Windows	Heavy Traffic?
1.	_____	__ min open ☐	closed☐	yes☐ no☐
2.	_____	__min open ☐	closed☐	yes☐ no☐
3.	_____	__ min open ☐	closed☐	yes☐ no☐
4.	_____	__min open ☐	closed☐	yes☐ no☐
5.	_____	__ min open ☐	closed☐	yes☐ no☐
6.	_____	__ min open ☐	closed☐	yes☐ no☐

12. **Have you worked at or visited any of the following businesses during the past 24 hours? (Check all that apply)**

Worked	Visited		Worked	Visited	
☐	☐	Painting	☐	☐	Dry cleaning

Worked	Visited		Worked	Visited	
☐	☐	Chemical/plastics plant	☐	☐	Petroleum plant (Oil sands)
☐	☐	Service station/garage	☐	☐	Furniture refinishing/repair
☐	☐	Wood processing plant	☐	☐	Printing
☐	☐	Hospital	☐	☐	Renovations/construction

13. **Have you performed any of the following activities during the past 24 hours?**
(Check all that apply)

☐ Metal work
☐ Welding
☐ Plumbing
☐ Plastics work
☐ Automotive or other mechanical repair
☐ Auto body repair
☐ Painting
☐ Gluing/caulking
☐ Furniture refinishing/repair
☐ Floor waxing/stripping
☐ Other renovations/redecorating – specify: _____
☐ Used degreasers
☐ Used air fresheners/deodorizer
☐ Used other cleaning products – specify: _____
☐ Scale model building
☐ Other hobbies/craft work
☐ Starting the car in the garage – specify fuel type:_____
☐ Other activities which may have led to exposure to chemicals:

_____
_____
_____
_____
_____
_____
_____

14. **Please indicate any other events during this time period which may have led to exposure to chemicals or airborne pollutants:**

_____
_____
_____
_____
_____
_____
_____

END OF QUESTIONNAIRE

FORT MCKAY AIR QUALITY STUDY
Household Activity Questionnaire (Q3)

Sample No: _____ Interviewer: _____

Date: ____ / ____ / ____

1. **Did you have your drapes, carpet, or furniture professionally cleaned during the past 4 days?**
   ☐ Yes ☐ No

2. **Did you vacuum your home during the past 4 days?**
   ☐ Yes ☐ No

3. **Were any windows or outside doors left open in your home during the past 4 days?**
   ☐ Yes ☐ No

4. **Have you or visitors used tobacco inside the home, in any form, during the past 4 days?**
   ☐ Yes (GO TO QUESTION 5) ☐ No (GO TO QUESTION 6)

5. **Which of the following tobacco products were used in the past 4 days?**
   ☐ Cigarettes ☐ Cigars ☐ Pipe

   Approximately how many cigarettes/cigars were smoked during the past 4 days? _____

6. **Did you generate any other smoke (forest or camp fires, smoke houses, etc.) at your residence during the past 4 days? If yes, please specify the source(s) of the smoke.**
   ☐ Yes (specify below) ☐ No
   Specify:
   _____

7. **Have you used insecticides, pesticides, or herbicides in the past 4 days?**
   ☐ Yes ☐ No

8. **Have you operated any gas-powered appliances or tools at your residence in the past 4 days? If specify the appliance or tool and type of fuel.**

☐ Yes (specify below) ☐ No

	Appliance/Tool	Fuel
1.	_____	_____
2.	_____	_____
3.	_____	_____

9. **Did you start your car in the garage in the last 4 days?**

☐ Yes ☐ No

If yes, what type of fuel does it uses?_____

10. **Did you use a portable fan or humidifier in the last 4 days?**

☐ Yes (specify below) ☐ No

Where?_____

11. **Did you use clothes dryer in the last 4 days?**

☐ Yes ☐ No

12. **Have you performed any of the following activities during the past 4 days at your residence?**

(Check all that apply)

☐ Metal work	☐indoor	☐outdoor
☐ Welding	☐indoor	☐outdoor
☐ Plumbing	☐indoor	☐outdoor
☐ Plastics work	☐indoor	☐outdoor
☐ Automotive or other mechanical repair	☐indoor	☐outdoor
☐ Auto body repair	☐indoor	☐outdoor
☐ Painting	☐indoor	☐outdoor
☐ Gluing/caulking	☐indoor	☐outdoor
☐ Furniture refinishing/repair	☐indoor	☐outdoor
☐ Floor waxing/strippping	☐indoor	☐outdoor
☐ Other renovations/redecorating – specify: _____	☐indoor	☐outdoor
☐ Used degreasers	☐indoor	☐outdoor
☐ Used air fresheners/deodorizers		
☐ Used other cleaning products – specify: _____	☐indoor	☐outdoor
☐ Scale model building	☐indoor	☐outdoor

☐ Other hobbies/craft work ☐indoor ☐outdoor

☐ Other activities which may have led to exposure to chemicals:

_____

_____

_____

13. **Do you have any of the following items? Where is it stored? Did you use it recently, and if so where? Please complete the below table.**

Item	Do you have? (y/n)	Storage location? (specify floor and room)	Recent use? (n/d/wk)	Where was recent use (if different from storage)? (specify floor and room)
Gas, oil				
Propane				
Other fuels				
Vehicles				
Rec. vehicles				
Pesticides/ Fertilizers				
Paint or varnish				
Solvents				
Glues				
Dirty work clothing				
Clean/disinf. Agents				
Air deodorant				
Mothballs				
Cosmetic/hair products				
Aerosol spray				
Office equip.				

14 **Please indicate any other events during this time period which may have led to exposure to chemicals or airborne pollutants:**

END OF QUESTIONNAIRE

Appendix C. Summary of SO_2 Sampling Data

Table C-1. Summary of blank SO_2 measurements.

Week	Sampler ID	House #	µg of sulphate/sampler
week 1	SO6598	H135	1.08
	SO6600	H135	0.64
week 2	SO6546	H94	1.03
	SO6599	H94	1.46
week 3	SO6639	H42D	0.69
	SO6572	H42D	0.48
week 4	SO6628	T48	0.52
	SO6669	T48	0.4
	SO6671	T40A	0.45
	SO6641	T40A	0.74

SD=	0.340831
Mean=	0.749
SE=	0.10778
Var=	0.116166

Table C-2. Summary of 96-hour TWA of co-located SO_2 measurements.

Week	Sampler ID	µg/m3	Time in	Date in	Time out	Date out
week 1	SO6581	0.18	5:45PM	9/23	7:30PM	9/27
	SO6575	0.24 (R)	5:45PM	9/23	7:30PM	9/27
	SO6592	0.39 (R)	5:45PM	9/23	7:30PM	9/27
week 2	SO6586	1.28	7:35PM	9/27	8:30PM	10/1
	SO6590	1.30 (R)	7:35PM	9/27	8:30PM	10/1
week 3	SO6647	2.71	8:27PM	10/4	6:59PM	10/12
	SO6630	2.58 (R)	8:29PM	10/4	6:58PM	10/12
	SO6679	2.76 (R)	8:28PM	10/4	6:59PM	10/12
week 4	SO6627	1.37	7:02PM	10/12	6:20PM	10/16
	SO6642	1.18 (R)	7:02PM	10/12	6:20PM	10/16
week 5	SO6670	2.04	6:40PM	10/17	6:12PM	10/21
	SO6622	2.23 (R)	6:40PM	10/17	6:12PM	10/21
	SO6643	2.12 (R)	6:40PM	10/17	6:12PM	10/21

(R)= Replicate

Table C-3. Summary of blind blanks SO_2 measurements.

Week	Sampler ID	µg/m3
week 2	SO6548	0.00
	SO6551	0.00
	SO6580	6.18
	SO6589	2.40
week 5	SO6635	0.11
	SO6649	0.12
	SO6655	0.00
	SO6674	0.17
	SO6678	0.00

Table C-4. Summary of 96-hour TWA of indoor SO_2 measurements.

Week	Sampler ID	House #	µg/m3	Time in	Date in	Time out	Date out
week 1	SO6602	H52	0.30	5:09PM	9/23	3:15PM	9/28
	SO6573	H135	0.38	4:41PM	9/25	4:40PM	9/1
	SO6556	H135	0.40 (R)	4:45PM	9/25	4:35PM	9/29
	SO6549	H41	0.15	6:00PM	9/26	6:05PM	9/30
week 2	SO6591	H10	0.13	6:50PM	9/27	12:02PM	10/1
	SO6571	H94	0.37	6:15PM	9/27	11:54AM	10/1
	SO6566	H94	1.01 (R)	6:15PM	9/27	11:54AM	10/1
	SO6583	H72	0.00	6:55PM	9/28	6:45PM	10/2
	SO6584	H72	0.00 (R)	6:55PM	9/28	6:48PM	10/2
	SO6576	H72	0.05 (R)	6:55PM	9/28	6:46PM	10/2
	SO6569	H119	0.12	7:00PM	9/29	5:20PM	10/3
	SO6593	T150	0.11	5:10PM	9/29	5:05PM	10/3
	SO6601	H54	0.50	7:46PM	9/30	6:49PM	10/4
	SO6564	T160	0.30	12:27PM	10/1	1:55PM	10/4
	SO6568	H45	0.42	7:50PM	10/1	5:24PM	10/5
	SO6588	H14	0.69	5:58PM	10/2	5:00PM	10/6
	SO6585	H14	0.89(R)	5:58PM	10/2	5:00PM	10/6
	SO6561	H40	0.00	7:05PM	10/2	4:45PM	10/6
	SO6552	T149	0.20	6:20PM	10/3	4:25PM	10/7
	SO6558	T108	0.37	7:10PM	10/3	5:32PM	10/7
week 3	SO6676	H42D	0.19	5:15PM	10/4	4:30PM	10/12
	SO6637	H42D	0.22 (R)	5:15PM	10/4	4:30PM	10/12
week 4	SO6675	H88	0.31	6:05PM	10/12	4:10PM	10/16
	SO6648	H206	1.21	5:35PM	10/12	5:45PM	10/16
	SO6634	H16	0.09	7:10PM	10/13	2.08PM	10/18
	SO6640	H16	0.13 (R)	7:10PM	10/13	2.09PM	10/18
	SO6646	H16	0.14 (R)	7:11PM	10/13	2:10PM	10/18
	SO6638	T201	0.39	5:14PM	10/14	4:35PM	10/18
	SO6623	H96A	0.20	7:15PM	10/14	6:42PM	10/18
	SO6656	T157	0.31	6:05PM	10/15	2:30PM	10/19
	SO6644	T157	0.33 (R)	6:06PM	10/15	2:30PM	10/19
	SO6657	H92A	0.98	5:15PM	10/15	4:10PM	10/19
	SO6645	H101	0.59	5:23PM	10/16	5:05PM	10/20
	SO6650	T48	0.92	4:30PM	10/16	4:30PM	10/20
	SO6631	H8	0.35	4:27PM	10/17	4:24PM	10/21
	SO6667	T162	0.34	5:12PM	10/17	4:35PM	10/21
	SO6663	T40A	1.12	6:09PM	10/17	5:39PM	10/21
	SO6672	T40A	0.82 (R)	6:10PM	10/17	5:39PM	10/21
week 5	SO6621	H102	0.40	5:45PM	10/18	4:30PM	10/22
	SO6673	T15A	0.46	6:12PM	10/18	4:03PM	10/22

(R)= Replicate

Table C-5. Summary of 96-hour TWA of outdoor SO_2 measurements.

Week	Sampler ID	House #	µg/m3	Time in	Date in	Time out	Date out
week 1	SO6560	H52	0.77	5:26PM	9/23	3:26PM	9/28
	SO6563	H135	1.7	5:05PM	9/25	4:50PM	9/29
	SO6595	H135	1.07 (R)	5:05PM	9/25	4:50PM	9/29
	SO6578	H41	9.54	6:20PM	9/26	6:10PM	9/30
week 2	SO6559	H10	0.83	7:09PM	9/27	12:10PM	10/1
	SO6567	H94	1.34	6:35PM	9/27	11:56AM	10/1
	SO6554	H94	2.20 (R)	6:35PM	9/27	11:56AM	10/1
	SO6550	H72	3.73	7:08PM	9/28	6:55PM	10/2
	SO6547	H72	28.86 (R)	7:08PM	9/28	6:55PM	10/2
	SO6597	H72	0.05 (R)	7:08PM	9/28	6:55PM	10/2
	SO6555	H119	0.84	7:20PM	9/29	5:25PM	10/3
	SO6596	T150	0.23	5:35PM	9/29	5:10PM	10/3
	SO6570	H54	0.74	7:55PM	9/30	7:00PM	10/4
	SO6594	T160	0.27	12:45PM	10/1	2:05PM	10/4
	SO6557	H45	0.41	8:15PM	10/1	5:30PM	10/5
	SO6553	H14	1.47	6:10PM	10/2	5:10 PM	10/6
	SO6587	H14	1.79 (R)	6:10PM	10/2	5:10PM	10/6
	SO6579	H40	1.32	7:15PM	10/2	4:50PM	10/6
	SO6562	T149	2.84	6:30PM	10/3	4:30PM	10/7
	SO6565	T108	2.73	7:20PM	10/3	5:43PM	10/7
week 3	SO6582	H42D	2.45	5:25PM	10/4	4:40PM	10/12
	SO6668	H42D	2.22 (R)	5:26PM	10/4	4:40PM	10/12
	SO6636	H88	1.43	6:15PM	10/12	4:08PM	10/16
week 4	SO6651	H206	0.75	5:48PM	10/12	5:49PM	10/16
	SO6626	H16	1.11	7:28PM	10/13	2:18PM	10/18
	SO6632	H16	1.26 (R)	7:30PM	10/13	2:19PM	10/18
	SO6664	H16	1.25 (R)	7:29PM	10/13	2:18PM	10/18
	SO6633	T201	3.63	5:33PM	10/14	4:43PM	10/18
	SO6659	H96A	1.95	7:35PM	10/14	6:45PM	10/18
	SO6658	T157	2.57	6:19PM	10/15	2:45PM	10/19
	SO6652	T157	2.32 (R)	6:20PM	10/15	2:45PM	10/19
	SO6665	H92A	1.83	5:32PM	10/15	4:16PM	10/19
	SO6661	H101	1.97	5:33PM	10/16	5:10PM	10/20
	SO6625	T48	2.35	4:50PM	10/16	4:34PM	10/20
	SO6660	H8	LOST	4:39PM	10/17	-	-
	SO6653	T162	1.52	5:27PM	10/17	4:45PM	10/21
	SO6677	T40A	1.55	6:16PM	10/17	5:45PM	10/21
	SO6654	T40A	1.58 (R)	6:17PM	10/17	5:45PM	10/21
week 5	SO6629	H102	2.66	6:00PM	10/18	4:35PM	10/22
	SO6666	T15A	2.47	6:31PM	10/18	4:10PM	10/22

(R)= Replicate

Appendix D. Daily Environmental Monitoring Station Data with Meteorological Conditions in Fort McKay

Table D-1. Summary of SO_2 measurements and meteorological data from Environmental Monitoring Station.

Date	WSP (km/hr)	WDR (degree)	RH (%)	Temp (K)	SO2 Conc (ppb)	SO2 Conc (µg/m3)
9/23	10.00	191.42	54.67	287.73	1.09	2.95
9/24	10.08	249.46	44.88	283.57	0.39	1.08
9/25	12.29	283.04	46.04	283.01	0.52	1.44
9/26	6.08	219.79	58.50	278.65	0.43	1.22
9/27	9.54	248.79	73.20	277.15	0.06	0.16
9/28	11.13	185.13	59.71	277.35	1.52	4.28
9/29	14.75	310.46	57.58	275.79	0.52	1.48
9/30	5.25	209.29	54.92	271.19	0.00	0.00
10/1	6.46	209.17	64.88	270.44	0.13	0.38
10/2	9.25	235.28	61.83	271.20	0.22	0.63
10/3	4.50	199.46	68.46	273.51	0.13	0.37
10/4	5.17	261.63	87.75	271.98	0.00	0.00
10/5	8.79	208.58	74.38	274.77	0.04	0.12
10/6	17.88	163.33	76.79	277.22	2.17	6.12
10/7	10.13	180.04	80.13	279.08	2.74	7.66
10/8	8.29	224.33	61.75	278.73	0.26	0.73
10/9	4.08	230.71	72.54	276.26	0.17	0.49
10/10	6.88	195.75	73.75	276.11	0.74	2.09
10/11	4.46	211.92	82.08	273.38	0.57	1.61
10/12	8.71	183.63	67.42	274.30	1.39	3.96
10/13	7.46	214.63	81.71	276.22	0.22	0.61
10/14	10.13	269.50	76.83	276.75	0.09	0.25
10/15	6.88	281.08	96.63	273.40	0.13	0.37
10/16	10.54	201.75	85.50	273.78	1.00	2.85
10/17	7.63	143.25	85.42	274.42	0.52	1.48
10/18	8.88	212.71	79.54	273.61	1.74	4.96
10/19	9.83	231.42	60.00	282.54	0.57	1.56
10/20	14.71	282.33	49.63	283.71	0.00	0.00
10/21	6.46	123.29	71.83	274.71	0.09	0.25
10/22	11.71	167.38	62.83	278.15	3.96	11.11

WSP = Wind Speed
WDR = Wind Direction
RH = Relative Humidity
Temp = Temperature

Appendix E. Environmental Monitoring Station with Outdoor SO_2 Data taken in Fort McKay

Table E-1. Summary of outdoor SO_2 measurements with Environmental Monitoring Station SO_2 measurements.

Date	Outdoor Conc (µg/m3)	Environmental Monitoring Station (µg/m3)
23 Sept -28 Sept	0.77	1.86
25 Sept-29 Sept	1.39	1.71
26 Sept -30 Sept	9.54	1.44
27 Sept -1Oct	0.83	1.28
27 Sept -1Oct	1.77	1.28
28 Sept -2 Oct	1.89	1.37
29 Sept- 3Oct	0.84	0.57
29 Sept- 3Oct	0.23	0.57
30 Sept 4 Oct	0.74	0.27
1Oct -4 Oct	0.27	0.34
1 Oct-5 Oct	0.41	0.30
2 Oct-6 Oct	1.63	1.46
2 Oct-6 Oct	1.32	1.46
3 Oct- 7 Oct	2.84	2.88
3 Oct- 7 Oct	2.73	2.88
4 Oct- 12 Oct	2.34	2.54
12 Oct- 16 Oct	1.43	1.61
12 Oct- 16 Oct	0.75	1.61
13 Oct -18 Oct	1.21	1.75
14 Oct-18 Oct	3.63	1.98
14 Oct-18 Oct	1.95	1.98
15 Oct- 19 Oct	2.45	2.24
15 Oct- 19 Oct	1.83	2.24
16 Oct -20 Oct	1.97	2.15
16 Oct -20 Oct	2.35	2.15
17 Oct- 21 Oct	1.52	1.64
17 Oct- 21 Oct	1.57	1.64
18 Oct -22 Oct	2.66	3.56
18 Oct -22 Oct	2.47	3.56

Appendix F. Air Exchange Results

Table F-1. Summary of air exchange measurements in Ft. McKay in late fall from 24 sampled households.

House Type	House ID	Air Exchange Rate-air changes per hour (ACH)				Averg (ACH)	Average Temp (deg Celcius)	House Vol (cu.ft)	perm rate ng/min
		CAT 1	CAT 2	CAT 3	CAT 4				
house	8	did not deploy PMCH or CATs	N/A	N/A	N/A	N/A	N/A	12000	N/A
house	10	lost in field	lost in field			lost in field	22.5	12000	-383.64
house	14	0.22	0.21			0.21	N/A	14400	-370.55
house	16	0.43	0.27			0.35	17.00	12480	-369.91
house	40	0.19	0.15			0.17	17.50	16000	-381.10
house	41	0.50	0.46			0.48	19.50	12000	-382.50
house	45	0.52	0.52			0.52	24.50	12000	-382.50
trailer	48	0.60	0.52			0.56	20.00	6400	-364.70
house	52	0.24	0.23			0.24	20.50	11200	-376.01
house	54	0 field blank	0 field blank	0.53	0.47	0.50	19.00	9600	-376.01
house	72	0.77	0.69			0.73	N/A	6000	-372.20
house	88	0.22	0.21			0.21	21.75	12000	-381.86
house	94	lost in field	lost in field			lost in field	N/A	12800	-373.47
house	101	0.27	0.19			0.23	18.00	15090	-383.26
house	102	0 field blank	0.16	0.15	0.15	0.15	20.00	14400	-371.31
trailer	108	0.54	0.44			0.49	19.00	7680	-369.40
house	119	0.55	0.54	0.53	0.50	0.53	20.00	10060	-363.68
house	135	0.60	0.57			0.58	21.50	9600	-364.70
trailer	149	0.23	0.22			0.23	22.50	9472	-370.04
trailer	150	lost in field	less than 0.03			less than 0.03	N/A	6400	-372.45 *
trailer	157	0.29	0.29			0.29	17.50	6720	-368.64
trailer	160	less than 0.01	less than 0.01			less than 0.01	23.00	6160	-373.98
trailer	162	0 field blank	0.71	0.71	0.63	0.68	18.50	6360	-378.56
trailer	201	0 field blank	0.37	0.37	0.35	0.36	22.50	6400	-371.31
house	206	0.33	0.29			0.31	23.00	9600	-378.56
trailer	15A	0.00	7.5 *	0.38	0.37	0.37	17.50	6400	-369.91
trailer	40A	did not deploy PMCH or CATs	N/A	N/A	N/A	N/A	N/A	8640	N/A
house	42D	0.20	0.18			0.19	23.50	12000	-354.26
house	92A	0.00	0.45	0.43	0.39	0.42	21.50	10462	-372.33
house	96A	0.55	0.41			0.48	22.75	12000	-370.55

*= Outlier
N/A= Not Available

Appendix G. Protocol for Air Exchange Measurement

PROTOCOL FOR AIR EXCHANGE MEASUREMENT

1. Scope

This document is intended to provide the necessary details for the determination of indoor/outdoor air exchange rates in relatively small enclosures such as homes, apartments, or small offices. Following the procedure below, air exchange rates can be quantified over the range 0.10 to 2.5 air changes per hour (ACH). The limit of detection is about 3.0 ACH.

2. Introduction

The measurement of air exchange rate (AER) is accomplished using a tracer gas under steady-state conditions, and a passive sampling technique followed by sample analysis with a gas chromatograph and electron capture detector (GC/ECD).

This method is based upon the technique developed by Dietz et al(1). An inert, non-toxic, tracer chemical, perfluorinated methylcyclohexane (PMCH), is allowed to permeate into the enclosure for 24 hours. During this period a steady-state concentration is theoretically established based upon partly the permeation rate of the PMCH source, the volume and temperature of the enclosure and its average air exchange rate. Now, the passive sampling device, a capillary adsorption tube (CAT), is located in the enclosure and allowed to collect PMCH for a fixed period of time ranging from 12 hours to one week. The PMCH permeation source remains in the enclosure for the duration of the sampling period. The passive sampling device is returned to the laboratory for determination of the amount of PMCH collected. Given the above variables, the collection rate of the CAT, and conversion factors, the average air exchange rate can be calculated. The PMCH source is removed one day after CAT sampling is complete, then it is returned to the lab for post-experimental permeation rate verification.

3. PMCH sources

PMCH sources have a nominal permeation rate of 375 ng/min. at 24-25 degrees C. and a useful lifetime of about 4-5 years. The permeation rate is proportional approximately to temperature, 3% per degree C. For a batch of sources prepared with the same materials at the same time the permeation rate has an associated relative standard deviation (RSD) less than 3%.

A) Preparation

Apparatus, Materials, Supplies:
22 mm aluminum bullet shells and holder
PMCH (Aldrich Chemical)
50 ml or 100 ml graduated glass beaker

autopipette for transferring 0.4 ml
silicone rubber solid tubing
aluminum plug-cutting tool
silicon high vacuum grease
crimper
7 mm punch
razor blades, single edge
electromechanical vibrating engraver or equivalent
lab tissue paper
disposable rubber gloves
#3 cork borer
polyurethane foam
labels 0.5cmx2.5cm
clear tape 3/4"

Procedure:

1. Engrave an ID on each bullet shell. The ID should be HSPH yy-nnn where yy are the last two digits of the year made and nnn is the next sequential number.
2. Using the punch and hammer, carefully expand the open end of each shell only slightly to facilitate later insertion of the silicone plug. Place the engraved shells sequentially in the shell holder.
3. Lay a piece of silicone rubber solid tubing in the aluminum plug jig and carefully cut fixed length plugs with a razor blade. Cut one plug for each source.
4. Using gloves, apply a very thin layer of silicone grease to the circumferential surface of the plugs being careful not to get grease on the flat surfaces.
5. Calculate the total ml of PMCH needed: number of PMCH sources multiplied by 0.4 ml per source.
6. Transfer the calculated amount of PMCH plus a small additional amount to the graduated glass beaker.
7. With the autopipette, transfer 0.4 ml PMCH to 6 shells.
8. Carefully insert/press a rubber plug into each shell until it is just flush with the top edge.
9. Crimp the plugged end of each shell with the special crimper tool.
10. Remove excess grease if any with a piece of tissue and replace the shell in the holder.
11. With a hack saw cut the polyurethane foam into blocks of 2cm(L) x 3cm(W) x 5cm(H).
12. Bore two holes: one, straight through the 3cm dimension at 4cm(H); the second hole to be also about 3cm long, but from the center of the just bored hole through the 5cm dimension, but not straight through.
13. Insert a source through the first 3cm hole into the second 3cm hole of the polyurethane plug so that the end of the source with the silicone rubber plug just barely protrudes into the first 3cm hole of the polyurethane plug .
14. Prepare a small label (0.5cmx2.5cm) with the ID of the PMCH source and attach it securely to the polyurethane plug with a piece of clear tape all the way around.

15. Repeat the process until all sources are made. Place them in a box and store beneath another vented hood away from any potential contact of PMCH with CATs.

B) Determination of permeation rate

Apparatus, Materials, Supplies:
PMCH permeation sources
Analytical balance with a readability/accuracy/precision of 0.1 mg.
Plastic tweezers
Worksheet template

Procedure:
1. The PMCH source must be at least 3 weeks old prior to any weighing.
2. On the template, record the date, time, and temperature. Record the IDs of the PMCH sources.
3. Make sure the balance pan is clean (gently wipe with a fine artist brush) and rezero the balance.
4. Using the plastic tweezers, carefully extract the PMCH source from its polyurethane block holder and place on the balance pan.
5. Allow the reading to stabilize and record the weight. A new source weighs between 1.8 and 2.0 gm. whereas one at the end of its useful life is usually at or below 1.2 gm.
6. Remove the source from the balance pan and replace it in the polyurethane holder.
7. Check the zero and reset if necessary.
8. Weigh 9 more sources, then reweigh one of the previous nine by random selection.
9. Continue this procedure until all PMCH sources have been weighed and recorded.
10. If the weighing session is the first time the sources have been weighed, then stop here.
11. If this is the second or a subsequent weighing, then the permeation rate may be calculated. For a newer source at least 3 weighing sessions about 2 weeks apart each, are necessary for confirmation of a constant permeation rate. Sources should be weighed twice each, before and after field deployment.
12. The permeation rate is calculated by taking the difference in two weights from different weighing sessions, multiplying by 10^{-9} to convert grams to nanograms, and dividing by the time interval in minutes.

$$R_P = [(W_{Tf} - W_{Ti}) * 10^{-9} \text{ (ng/gm)}] / [(Tf - Ti) \times K] \quad (1)$$

where

R_P = Permeation Rate in ng/ml
W_{Tf} = final weight of permeation source in gm.
W_{Ti} = initial weight of permeation source in gm
Tf = date and time of final weighing
Ti = date and time of initial weighing

K = factor for converting days to minutes (1440 minutes/day) and/or hours (60 minutes/hour)

13. General example/discussion: a total of 4 weighing sessions, 2 before and 2 after. Assuming the temperature to be 24 degrees C. for the interval between the first two sessions and the last 2 sessions, the permeation rate should reflect the same equilibrium conditions and be the same within experimental error. The permeation rate between the 2nd and 3rd weighing sessions represents the time interval during field deployment. Providing the temperature remained at 24 degrees C. and there was no mishandling of sources, the permeation rate should be the same as that measured in the lab. (Sources returned from the field should be weighed as soon as possible.) Any change in the permeation rate should obviously be consistent with field temperatures.

Permeation rate for the field at other than 24 degrees C. should also be calculated by applying the appropriate temperature correction factor to the lab measured rate, i.e. the rate obtained from the 1st/2nd and/or 3rd/4th session. The corrected rate should be close to the rate calculated for the 2nd/3rd session rate. When using the permeation rate for the AER calculation, select the rate which is most consistent with actual source history. For this one may consider that to reach a new permeation equilibrium at a different temperature, takes only a day or two compared to the 3 week duration needed for newly prepared sources. For homes where there is a diurnal variation in temperature, make the correction based on the average temperature determined by max-min thermometers.

4. Cleaning of CATs

The CAT sampling device consists of a short length of glass tubing (6.35 cm L x 0.6cm OD x 0.4cm ID) containing a small amount of a carbonized adsorbing material which is sandwiched in the middle by stainless steel screens. An identification number (ID) is permanently engraved on each sampler. The ends of the CAT are capped with either a polyurethane cap or a polyethylene cap. CATs are cleaned by thermally desorbing any adsorbed compounds from them at an elevated temperature in an inert nitrogen atmosphere.

Apparatus, Materials, Supplies:

23 position cleaning rack with attached nichrome heating coils
variable voltage transformer
low voltage, high current transformer
automatic programmable shut off timer (1500 watt)
ultrahighpurity nitrogen gas (tank with pressure regulator and needle valve)
standard lab tubing (rubber or polyethylene) to connect the gas tank/valves to the rack
flowmeter, 500 ml/min
carbon paper and/or activated charcoal tea bags
cleaning worksheet template
resealable plastic bag

Procedure:

1. On the worksheet, enter your name, date of cleaning, and IDs of CATs. Note any unusual CATs.
2. Remove the protective caps from 23 CATs and insert the CATS through the coils into the rack's retaining silicone O-rings. The rack is on the upper shelf of the cabinet below the fume hood. Make it protrude a few inches by sliding it toward the operator.
3. Turn on the nitrogen gas tank valve, adjust the pressure regulator to about 10 psi.
4. Attach a flowmeter to any of the 23 CATs and adjust the needle valve for a flow of about 15 ml/min.
5. Check the flow in the remaining 22 CATs to be in the range of 10-100 ml/min.
6. Remove the flowmeter.
7. With the variable voltage transformer set to zero, turn on the timer:
   A. Press the *T1*
   B. Press the *min* button until 25 has registered.
   C. Press *Outlet 1* to activate the outlet, red light on.
   D. Slowly turns the variable voltage transformer dial to a reading of 80. This should produce a just barely visible red-orange glow in the heating coils.
   E. Press *Start* on the timer.
8. After 25 minutes have elapsed, the timer automatically shuts off voltage to the variable voltage transformer. Allow about 15 more minutes for the heating coils to cool.
9. Replace the protective caps on 22 of the 23 CATs.
10. Turn off the nitrogen gas tank main valve, pressure regulator, and needle valve.
11. Remove the 23rd CAT with no cap and recap at both ends.
12. Remove the 22nd CAT and recap the one open end.
13. Proceed in similar fashion until all the CATs have been removed and recapped. Minimize the time spent doing this to reduce the amount of air that can diffuse into the CAT.
14. Place all the CATs in a plastic resealable bag containing protective carbon paper or 2 activated charcoal tea bags.
15. Label the bag: number of CATs, date cleaned, and initials. Store in a labeled drawer.
16. Place the worksheet in the Clean/QC file.
17. Allow the rack to cool down.
18. Replace the rack in its original position.

Safety: Perform this work in the fume hood area with no combustible solvents nearby. Attach a sign in a convenient location to indicate the high temperature hazard.

5. Quality Assurance

Apparatus, Materials, Supplies:
23 cleaned CATs
special gas chromatograph with autosampler and integrator (described below)

silicone grease
disposable latex gloves (non-powdered)

For most projects, all CATs are analyzed before being sent out to the field. For projects with many CATs (>500) each bag of 23 CATs is at least subsampled to check for contamination. The size of the subsample may vary but may never be less than 3 CATs (10%).

Upon QA analysis, CATs must have < 1.0 pl PMCH, or a peak at t_r~1.3 minutes with an area count < ~50000 counts. The actual area count must be determined by first establishing the value for 1.0 pl. This is easily done by determining the area count for a lab blank (=0.0 pl) and a standard PMCH in the range of 2.0 pl. If the CAT has < 5 pl PMCH (as measured from a recent standard curve) then it can be rerun. If the rerun is < 1.0 pl PMCH, then the CAT may be accepted, otherwise it must be recleaned by the usual process. All data and information must be recorded on the cleaning worksheet and the CAT QA worksheet. Follow the same procedure for CAT analysis (described below):

A) Preparation of Standard CATs (for analysis)

Purpose and Design:
A series of CATs are prepared with known amounts of PMCH (and optionally PDCH). Each analytical run of samples is accompanied by a full set of CAT standards covering the range of nterest of PMCH. The standards are used to construct calibration curves for calculating the amount of PMCH in unknown samples.

A PMCH generator is used. It consists of a source of inert nitrogen gas flowing over a temperature-controlled PMCH source. Flow is measured by a soap-bubble flowmeter and temperature controlled by a constant temperature water bath. Aliquots of PMCH vapor in nitrogen are removed sequentially with a series of gas-tight syringes of increasing volumes through a T-septum arrangement downstream of the generator.

Apparatus, Materials, Supplies:
Ultrahigh purity nitrogen gas tank with regulator, 20 µm id glass capillary and holder, and connecting tubing.
Cleaned and QA'd CATs
Temperature controlled water bath and copper tubing
20 ml midget impinger
Chronometer or stopwatch
50 ml burette class A
glass T
tubing
soap bubble solution
gas-tight syringes: 10, 25, 50, 100, 250, and 500 µl.

charcoal paper or charcoal tea bags

Procedure:

1. Determine the nitrogen flowrate
   Increase the regulator adjustment so that the secondary pressure is about 20 psi which corresponds to a flow of about 30 ml/min. Squeeze the bulb at the bottom of the glass tee to set in motion a soap bubble in the buret. When the bubble intersects the 50 ml line, start the chronometer; when the bubble intersects the 40 ml line, stop the chronometer. Record the elapsed time in seconds. Repeat two more times. Using the average of the 3 time readings calculate the nitrogen flow rate:

F (ml/min) = (10 ml x 60 sec/min) / average time (sec) (2)

2. Reweigh the standard PMCH source in the midget impinger at least once per month and use equation (1) to calculate the standard PMCH source permeation weight, $r_{p\text{-}std}$ and record all data and information on the standard CAT worksheet.
3. Calculate the concentration of PMCH in the generator:

PMCH (pl/µl) = [$r_{p\text{-}std}$ (ng/min) x (24.45 nl /350 ng) x1000 pl/nl] / [F (ml/min) x 1000 µl/ml] (3)

where

(350 ng/24.45 nl) is a molecular weight-molecular volume conversion factor. when $_{p\text{-}std}$ = 375 and F = 30, then PMCH (pl/µl) = 0.87 pl/µl.

4. Assemble from 1 to 9 sets of cleaned and QA'd CATs. Each set has 9 CATs. Every CAT must have an orange-brown silicone septum on the numbered end and on the plain end a black polyurethane cap or a red polyethylene Caplug, no. #EC-4. Record the CAT IDs on the Standard CATs worksheet.
5. Add the indicated µl of PMCH from the generator to the designated CATS using the syringe shown below:

amount of PMCH to be added:	syringe
0 µl	10 µl syringe
2 µl	10 µl syringe
4 µl	10 µl syringe
10 µl	25 µl syringe
20 µl	50 µl syringe
40 µl	100 µl syringe
100 µl	250 µl syringe
200 µl	500 µl syringe
0 µl	500 µl syringe

A. Check each syringe-needle for blockage by withdrawing the needle to about 80% of syringe volume, placing the needle tip in a beaker of water, and depressing the plunger. Look for air bubbles and remove the needle from the water while still depressing the plunger. Wipe the tip with lab tissue. If there is blockage, determine whether it's in the needle or the polytetrafluoroethylene (PTFE) needle retainer. Clean the former with the supplied wire. Clean the latter with the plunger. Be very careful not to deform, damage, or lose any parts. Use a low-power stereomicroscope if necessary.
B. For each of the "0" CATs pierce the CAT septum with the clean empty 10 µl syringe-needle, remove the needle and return the CAT to its storage position.
C. Repeat B. but with the clean empty 500 µl syringe-needle.
D. For the "2" to "20" CATs, insert the appropriate size syringe/needle into the metal T-septum on the PMCH generator and slowly "pump" the plunger at least 3 times. Set the plunger so that the PTFE tip end intersects the appropriate volumetric marking on the syringe. Withdraw the syringe from the generator septum.
E. Insert the syringe needle through the correspondingly appropriate standard CAT septum until the needle is within 5mm of the SS screen, and slowly depress the plunger all the way.
F. Remove the syringe needle and replace the CAT in its designated location.
G. Repeat D. through F. until all "2" to "20" standard CATs have been prepared.
H. For the "40" to "200" CATs, follow the same procedure as above except first withdraw air from the CAT before introducing the PMCH. This prevents pressure buildup and septum loosening. The amount of air to withdraw is twice the amount of standard PMCH to be introduced. E.g. withdraw 80 µl when preparing the 40 µl standard CAT.
I. Place some charcoal paper or charcoal tea bags in the standard CAT box , close, and store for at least 4 hours before using.
J. Make sure that all information has been recorded and store the worksheet in the file.

6. GC-ECD analysis of CATs

Introduction:
The amount of PMCH adsorbed on CATs is determined by GC-ECD analysis. A very complete discussion of the GC (Varian Model 6000) and the technique can be found in Dietz, R. et al. This discussion is strictly limited to the operation of the system at HSPH.

Apparatus, Materials, Supplies:
Varian GC with ECD; GC heavily modified in semi-multi-dimensional configuration for analysis of PMCH.
Hewlett-Packard 3393A integrator
5% H_2 and 95% N_2 carrier gas
Strip chart recorders: 0-1 mv, 0-2 mv, 0-5 mv, and 0-10 mv.

Custom in-house built 23 sample-position autosampler
Chrontrol Lab Timer-Electrical Controller for 1 or 2 circuits.
Silicone grease
Q-tips
Lab supplies/expendables, e.g. tissues gloves, etc.
Analysis worksheets from templates.

Carrier gas is 5% H_2 and 95% N_2. House supplied air is regulated to 30 psi and provides the air pressure necessary for operation of the 4 6-port switching valves integrally located on the GC, and for maintaining a tight seal on the autosampler's 24-port switching valve (op cit).

A Hewlett-Packard 3393A integrator is attached to the integrator signal lead of the GC. The integrator parameters and Basic language have been used to automate data acquisition and preliminary data reduction.
Further signal acquisition is obtained on a strip chart using the GC recorder signal. Also the temperature of the special external Porapak GC column (op. cit.) is monitored by a thermocouple with the signal (0-2 mv)displayed on a stripchart recorder.

Procedure:
Autosampler

1. Enter CAT ID data on the GC Analysis worksheet; i.e. autosampler rack position, a number between 1 and 23, the corresponding CAT ID, and the type of CAT, standard (std) or field sample (unknown,). Every run must have all 9 standard CATs necessary to construct a standard curve. Also every one must have at least one(1) lab blank and/or field blank. A Run will have then either 12 or 13 unknown CATs .
2. Remove the cam adjusters and the top plate from the rack
3. Loosen the C-clamps on the bottom plate of the rack
4. Use gloves. Apply a small amount of silicone grease to a Q-tip (or equivalent). Carefully and lightly use the Q-tip to apply the grease to the red silicone O-rings in the bottom plate. Clear any visible excesses. The grease facilitates the insertion of the CATs into the O-rings. The 0-rings on the top plate must be greased only once every week.
5. Remove the cap from the plain unnumbered side of each CAT and insure that the top cap is not very tight
6. Insert the 23 CATs with the ID facing up, through the heating coils into the O-rings according to the sequence on the worksheet. Press firmly but do not force which can cause breakage. Adjust the C-clamps firmly but not too tightly
7. Replace the top plate carefully; line up the top of the CATs with the wells on the top plate and press it firmly down to seat barely the CATs.
8. Insert the cam adjusters holding the arm in the 3 o'clock position. Replace an finger-tighten the nuts on the cam-adjusting screw

9. Rotate the cam-adjusting arms counterclockwise slowly and carefully to set the CATs and seal the O-rings. Use care so as not to break anything.
10. Attach the bungee cord to the cam-adjusting arms to prevent the arms from loosening.
11. Check the autosampler's LED reading for position. If not (00) use the toggle switch on the respective controller to reset it to 0.00

GC Procedure:

1. Check the A and B pressures on the right side of the instrument. The gauges should be pointing to the preset marks of 42 psi and 80 psi. The carrier gas pressure must be 80 psi as measured on the tank's regulator gauge
2. Insure that the integrator is in BASIC mode. Press "R" (for run) then "ENTER:. Follow the instruction on the integrator. When it prints "start pending" PROCEED.
3. Place the recorder ON/OFF toggle switch in the ON position. Activate the timer by pressing "CIRCUIT", "1", "ON", PROGRAM ", "1", "ON" .
4. On the left side of the GC, press "SCHEDULE". Set the mode for "SINGLE PASS", if necessary. Repeatedly press "ENTER" to get to line 1 and enter "2" for the method # and "24" for the number of injections. Press the "ENTER: button, then "INSTRUMENT STATUS" A. Finally press "START" to initiate the run.
5. The run will go for about 3.5 hours. Check the progress frequently to make sure the instruments are functioning properly and the area counts for standards and blanks are in the proper range .
6. When the run has been completed, remove the strip chart and the integrator chart and place them in a labeled file folder along with the GC analysis worksheet.
7. Remove the CATs from the autosampler by reversing the procedure above.
8. Recap the CATs and set them in the bin for cleaning.

Parameters for GC:
Oven temperature = 130 °C.
Oven temperature limit = 150 °C.
Run time = 8.5 minutes

Inj A temperature = 200 °C.
Inj B temperature = 200 °C.
Ion temperature (ECD) = 250 °C.
TCD temperature = OFF
Detector = 4 (ECD)
Range 10 (only two choices, 1 or 10)
Attenuation = 32 (0.1,1,2,4,8,16,32,64,128,256,512,1024)
AutoZero A ON
AutoZero B ON

Relay Settings:
Time Relays ON Relays OFF

0.01	3456	1278
0.25	12	
0.41		5
2.01	7	16
2.02		7
4.01	8	23
4.61	3	8

Parameters for Integrator operational settings.
Program of Integrator data reduction.
Program for Chrontrol Timer which controls the recorder pens.

To reset, the timer-controller should be disconnected from the wall outlet for at least one minute. Then perform the following key entry procedures:
TIME
ENTER
1
ENTER
CIRCUIT
1
OFF
INTERVAL
3
4
5
ENTER
ENTER
ENTER
TIME

To test the timer operation, first set up the program by pressing

TIME
ENTER
1
ENTER
CIRCUIT
1
ENTER
OFF
INTERVAL

after INTERVAL press
0
SEC

5
ENTER
TIME

to set the timer for a 5 second shutdown. To test, press
CIRCUIT
1
ON

and the circuit 1 indicator lamp should light.
Then press
PROGRAM
1
ON

at which time there should be a barely noticeable blink of the display; after 5 seconds, there should be an audible clicking sound simultaneous with the circuit 1 lamp light extinguishing. If this does not happen, then try reentering the program. When the test is successful, repeat the key entry procedure above entering 345 instead of the SEC 5 after the INTERVAL.

7. Calculations

A) Standard Curve

There is a spreadsheet template for entering the area counts from the integrator. It is straightforward and produces the calculated data for the unknowns. The replacement equations used in the template are very complex and it is suggested not to alter them. They are designed to produce a point-to-point fit for the standard curve. The curve's shape tends toward a quadratic as long as the amount of PMCH does not exceed about 400 picoliters. Note that the PMCH standard curve is not linear and so linear regression analysis (least squares analysis) cannot be used successfully across the entire range of interest.

Short of the template, one can devise their own spreadsheet as follows. Let the pl of PMCH from the standard CATs be the Y values and the area counts from the integrator be the X values. Enter these values in a spreadsheet which can perform either a quadratic fit or a point-to-point linear fit (sometimes termed a piecewise fit). Cubic may also work. The spreadsheet should be able to draw the standard curve and calculate the values of X for given values of Y.

Preparation of Standard Curve:
From the PMCH source permeation rate and the measured nitrogen flow from the PMCH generator, calculate the PMCH concentration(pl/µl) of the standards used as described earlier. Enter this value into the designated cell in the spreadsheet. Enter the corresponding area counts into the designated cell(s) in the spreadsheet.

[Alternatively, multiply the PMCH concentration by the percent of PMCH in the reagent (usually 90%). Multiply this by the volume(µl) of gas used for each standard to get the total amount of PMCH.]

Calculation of PMCH in Unknowns:
For the complete run, enter the sample (standard) ID and the corresponding integrator area counts into designated cells in the spreadsheet. **SHOW AN EXAMPLE** Now, the final data appears in the adjoining cells and the standard curve can be seen in the nearby chart

The concentration of PMCH in unknowns is calculated from the unknown area counts, the amount of PMCH in the standard with next least area counts, and the slope for the corresponding area count point on the standard. The slope is obtained either from the point-to-point fit or the quadratic equation. **IS THIS CLEAR OR CONFUSING?**

Organization of Files and Worksheets **SHOW EXAMPLES**

Worksheets
Source Permeation Rates
Cleaned CATs
QA'd CATs
Standard CATs
Files
GC Analyses
Sources
CATs
Clean
QA'd
Computer
Sources
Templates
Clean and Run
Standards
Special Runs
Data and Results
Shipping Procedures
Sources

8. Sources

A) Sources
Sources and CATs should never be transported together nor on the same day. Sources should be shipped in resealable plastic bags in a box within a box. Their value is

usually listed at $0.50 to $1.00 each. Paper records should be maintained showing what carrier, when, and the airbill or waybill number.

B) CATs

CATs are in resealable plastic bags with charcoal protection. These bags must be placed with charcoal paper or equivalent in a box within box for shipping. The declared value is $1.00 each. Boxes for shipping should be adequately cushioned and taped with 3" postal tape or equivalent.

9. Field Sampling

Introduction:

As with any chemical determination, the data are only as good as the sample. PFT AER is a passive technique operating in a possibly heterogeneous sampling theater. So, attention to numbers of sources and CATs as well as careful placement of PMCH sources and CATs are very probably the most important parts of the AER protocol.

A) Determination of the Number of Sources

The number of sources is determined by rearrangement of Equation

$$AER = (N * R_{Perm} * R_{CAT} * T_{CAT}) / (V_{PMCH} * V_{house})$$

and obtaining:

$$N = [AER * (V_{PMCH} * V_{house})] / (R_{Perm} * R_{CAT} * T_{CAT})$$

where

N = number of PFT sources used
R_{Perm} = PFT permeation rate in ng/min
R_{CAT} = CAT collection rate in liters/hr = 0.00838
T_{CAT} = CAT exposure time in min
V_{PMCH} = picoliters of PMCH found on CAT (GC analysis)
V_{house} = house volume in cubic feet
and conversion factors:
60 min/hr
28.3 lit/cubic foot
1,000,000,000 ng /gm
1000 picoliters/nanoliter
PMCH molecular weight = 350 gm/mole or ng/nmole
PMCH molecular volume = 24.45 lit/mole or nl/nmole

A desirable amount of PMCH to collect on a CAT is in the range of 20-100 µl. The sampling time is determined according to convenience, subjective assessment, and consideration of other simultaneous sampling.

To calculate the number of sources needed in a given location, using an estimate of 0.2 air changes per hour and an average R_{Perm} = 300 ng/min and a house volume of 6,048 cubic feet, with an exposure of 24 hours, then to collect 25 pl PMCH,

$N = [AER \bullet (V_{PMCH} \bullet V_{house})] / (R_{Perm} \bullet R_{CAT} \bullet T_{CAT})$ or

N = [0.2 air changes per hour • (25 pl • 6048 cubic feet • (28.3 lit/cubic foot)] / (300 ng/min • {24.5 nl/350 ng}• (1000 pl/nl) • 0.008308 lit/hr •24 hr • 60 min/hr)

N = 2 sources.

B) Determination of the Number of CATs

The number of CATs to be employed is determined according to the type of information desired. For average air exchange rate, as few as 1 or 2 CATs can be used if optimally placed. For a more accurate measure of average air exchange rate, CATs may be located in every room in the house or building. If one wants to know the AER for a given room, then 2 or more CATs may be placed there as well as a PMCH source. This can get very complex very quickly when one considers that air exchange occurs not only with the outdoors through window areas, but also within the home through the door. In this case it is best to employ another tracer, say PDCH, in a nearby hallway to determine the rate of inflow of air into the target room from the hallway, i.e. some measure of the air exchange between hallway and target room. This should be complemented by placing CATs in the hallway to measure the PMCH and thus get an independent measure of outflow of air into the hallway. Some of these issues are discussed in detail in references 1 and 2.

In addition to the above, there should be at least 10% duplicate CATs and 10% Field Blanks.

C) Locating Sources and CATs

As can be seen from the immediately preceding paragraph, the optimal positioning of sources and CATs is necessary to obtain the most meaningful AER data. A complete discussion is beyond the scope of this document.

Some general considerations can be stated however. Sources and CATs should be placed in areas which allow relatively free but not forced movement of air. CATs should be as close as reasonably possible to the breathing height for both sitting and standing and be in an area which is representative of where occupants sit or stand, and representative of the AER in that room. This is obviously a very subjective judgement in the absence of additional instrumentation. Sources should be in an area that allows the tracer to disperse evenly and be transported in the dwelling to all locations which influence the AER.

Among the areas to avoid are windows and doors where there are strong drafts or winds, stairways which have increased vertical air movement due to thermal effects,

adjacent to walls or in "cubbyholes", and away from sources of heat or cold, and appliances such as refrigerators and dehumidifiers which contain Freons, a potential interferent in the analysis.

It is good for CATs to be suspended if possible, or placed on a flat surface with the exposed end protruding beyond the end of the surface, e.g. a table or mantle or bookcase or bureau.

D) Deploying Sources and CATs

The sources are contained in polyurethane blocks and should never be touched or removed. There is one source per block. Sources are sent to the field in resealable plastic bags. They are never shipped or transported together anywhere with CATs particularly regarding the sampling location. Sometimes some charcoal is placed with the sources. The charcoal absorbs the PMCH so that it cannot escape or contaminate anything. Every block has an external ID which matches the source contained within. Sources can be secured by taping (removable type adhesive tape) or tying with a string (using the available hole in the block). Dental floss is a very convenient material for the latter. Orientation, though not the most important issue, should still be considered: try to secure so the ID is in readable position. Record the date, time, and location (include a sketch) on the sample data sheet.

The CAT samplers are packaged 5 to a resealable plastic bag; they should always be protected by charcoal, paper, tea bag, or equivalent. CATs are set out 24 hours or longer after the sources have been deployed. They can be taped (removable type adhesive tape) or secured with a wire or plastic tie, or tied with dental floss. They should never be closer than six (6) feet from a PMCH source. Once the location is selected and the CAT secured, the sampling CAT is "activated" by removing the cap on the numbered end and positioning it by having the open end facing down, to minimize collection of particles. Record the date, time, and location of the CAT on the sample data sheet.

E) Field Blanks

Field Blanks (CATs) are transported to the sampling location, and treated identically to unknowns except they are opened then immediately closed. They should be protected by charcoal paper or tea bags, replaced in the plastic bag, and left at the house if convenient, otherwise taken to the local field office or equivalent where there is no source of unprotected PMCH.

F) Duplicates

Duplicate CATs are used to establish precision. They are prepared and treated identically to the main CAT. They should be placed next to the main CAT within about 3-6 inches. Both duplicates and Field Blanks should be recorded on the sample data sheet.